

# Catalysis by metal nanoparticles supported on functional organic polymers

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## Abstract

The preparation and catalytic applications of dispersed metal catalysts supported on organic functional polymers are presented. The advantages of these catalysts, such as the easy tailoring with respect to the nature of the used support, the “nanoscale” size control of metal crystallites by the polymer framework, the high accessibility and consequent catalytic activity in a proper liquid or liquid–vapor reaction systems are stressed. Various proposed catalytic processes making use of these materials are presented and evaluated, including multifunctional catalysis, e.g. redox-acid. Interesting peculiar aspects such as the enhancement of the hydrogenation rate by nitrogen containing moieties anchored to the polymer backbone are emphasised. When suitable, a comparison with catalysts based on inorganic supports is given. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Metal nanoparticles are objects of great interest in modern chemistry and materials research, where they

find application in such diverse fields as photochemistry, nanoelectronics, optics, and catalysis [1–7]. In fact, often enough these particles do possess physical as well as chemical properties, which are distinct both from the bulk phase and from isolated atoms and molecules. Moreover, such unique features of metal nanoparticles appear to be significantly influenced by parameters such as the metal nanoparticle size, the organisation of the nanoparticle crystal lattice (i.e. the nature and amount of defects) and the chemical nature of the microenvironment surrounding the nanoparticle. Thus, there is a large potential for the development and application of metal nanoparticles with tailored physical and chemical properties in both catalysis and material science.

In the frame of this review, we shall concentrate on the utilisation of metal nanoparticles in catalysis. In

*Abbreviations:* APSDVB, tetraalkylammonium PSDVB; CAL, cinnamaldehyde; CAn, chloroaniline; CNB, chloronitrobenzene; COL, cinnamyl alcohol; DAA, diacetone alcohol; Et, ethyl; 2-EtAQ, 2-ethylantraquinone; 2-EtHQ, 2-ethylantrahydroquinone; EXAFS, extended X-ray absorption fine structure spectroscopy; MA, methacrylic acid; Me, methyl; MEFO, melamino-formaldehyde resin; MIBK, methylisobutyl ketone; MSO, mesithyl oxide; MTBE, methyl-*tert*-butyl ether; PS, poly-styrene; PSDVB, poly-styrene-co-divinylbenzene; PVP, poly-*N*-vinyl-2-pyrrolidone; SPSPDVB, sulphonated PSDVB; TOF, turnover frequency; XPS, X-ray photoelectron spectroscopy; XRMA, X-ray microprobe analysis

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particular, we will focus on the application of metal nanoparticles supported on organic functional polymers. The polymer support can be a soluble linear or branched macromolecule or a micellar aggregate which “wraps” the metal nanoparticle in solution, thus, preventing metal sintering and precipitation. On the other hand, it can be a *resin*, i.e. an insoluble material consisting in a bundle of physically and/or chemically cross-linked polymer chains in which the metal nanoparticles are embedded. There appears to be no sharp boundary between these two typologies of polymer supports. For example, it is possible to prepare soluble cross-linked polymers (“microgels”), which have been reported to effectively stabilise metal nanoparticles [8–10]. Furthermore, metal colloids protected by soluble linear polymers have been conveniently grafted onto insoluble resin supports to yield insoluble catalysts [11]. This review will be mainly devoted to metal nanoparticles on insoluble resin supports, since the area of soluble polymers as stabilisers for metal colloids has already been the object of thorough review [5]<sup>3</sup>. Hereafter, the word “polymer” will be used in a general sense, whereas the word “resin” will be employed to stress a polymer (usually cross-linked) insoluble in any common solvent.

The industrial application of catalysts based on functional resins, has thus, far largely been confined to acid catalysis [12], the production of methyl-*tert*-butyl ether (MTBE) being the most renowned example. The resins employed for this purpose are mainly SPSPVB copolymers. Other applications of functional resins in the field of catalysis include their use as supports for enzymes in some biocatalytic processes, e.g. the Nitto process for acrylamide synthesis [13]. In addition, there is a huge amount of literature on the use of functional resins as supports for transition metal complex catalysts (“hybrid” catalysts) [14,15]. In spite of the fact that up to now no large-scale process based on hybrid catalysts has reached commercialisation, the academic and industrial research in this field is still lively, particular attention being currently paid to the immobilisation of costly asymmetric catalysts.

Resin-supported metal nanoparticles are currently being employed as catalysts in some smaller scale industrial processes. Thus, strongly acidic ion-exchange resins are used as active supports for metal palladium

in the preparation of bifunctional catalysts comprising acid as well as hydrogenation-active centres. Such catalysts are employed, e.g. in the industrial synthesis of methylisobutyl ketone (MIBK) (Bayer catalyst OC 1038) [16,17], where the acid centres catalyse the dimerisation of acetone to diacetone alcohol (DAA) and its dehydration to mesityl oxide, which is then hydrogenated on the metal surface to the end product. Similar catalysts based on anion exchange resins (Bayer catalysts K 6333 and VP OC 1063) [16] are employed in industrial heat-exchange units for the reduction of dioxygen level in water from ppm to ppb. Other applications include an alternative route to MTBE (EC Erdölchemie process) [17,18] and the etherification–hydrogenation of mixtures of unsaturated hydrocarbons to give blends of alkanes and branched ethers for the manufacture of unleaded petrol (BP Etherol Process) [18].

In the above-mentioned applications, the resins are generally used as beads (0.2–1.25 mm diameter) or powders, in fixed-bed or suspension reactors (often operated batchwise) or, more frequently, in flow-through reactors. Working temperatures range from room temperature up to about 120°C. Most resin materials suffer from relatively low mechanical, thermal and chemical stability, which represents the main drawback of these supports in comparison to more traditional inorganic materials. For this reason, resin-based catalysts are mainly applied as fixed-beds; alternatively, special technical solutions are sometimes needed in order to cope with this problem [19,20]. On the other hand, resin supports do have other advantages in comparison to conventional supports. As we will see in more detail below, this stems from the fact that in functional resins the majority of the functional groups is embedded *inside* the polymer matrix, and not simply on the surface of the support particles, as it is commonly the case with inorganic supports. Even when permanent pores with high surface area are present in the resin, only a negligible fraction of the functional groups is truly positioned on the pore walls. Thus, when the resin is in the dry state, most of the catalytically active groups are located in the *glassy* polymer matrix and are inaccessible to reactant molecules. They become accessible when the resin is *swollen* by a suitable liquid medium having a good compatibility with the polymer, but even under these conditions they are still surrounded by a medium having a relatively high

<sup>3</sup> See the chapter written by J.S. Bradley in [1,46].

“concentration” of polymer chains from the support. This particular situation can advantageously affect the reactivity of the supported catalysts, e.g.

1. the concentration of reagents and products inside the swollen resin can be significantly different in respect to that in the bulk solvent, with potentially beneficial effects on catalyst specificity and selectivity;
2. equilibrium reactions taking place within the resin can be conveniently shifted to the right if the products have a low compatibility with the resin, and are therefore, expelled therefrom;
3. the kinetics of a given reaction can be substantially influenced by the microenvironment inside the swollen resin, thus, making it possible to change the preferred reaction pathway in comparison to the bulk solution;
4. size-selectivity effects are possible when reagents with different solvated dynamic radii are used simultaneously.

In connection with metal nanoparticles as the catalytically active moieties, the use of functional resins as supports offers some further convenient features, namely

5. it allows the generation of metal nanoparticles with a controlled size and size distribution;
6. it provides a mean to influence the chemical behaviour of the metal nanoparticles through the direct interaction of the metal surface with the polymer-bound functional groups.

The aim of this paper is to provide the reader with a thorough account of the state of the art in the field of catalysis with polymer-supported metal nanoparticles. Whenever possible, comparisons will be traced between the performance in a given reaction of polymer-supported catalysts and of catalysts based on more conventional supports like carbon or inorganic oxides.

## 2. Preparation of metal nanoparticles supported on functional polymers

The preparation of polymer-supported metal nanoparticles can be carried out along different routes, which are briefly outlined in Fig. 1.

Basically, the synthetic route involves three steps, namely (1) synthesis of a suitably functionalised

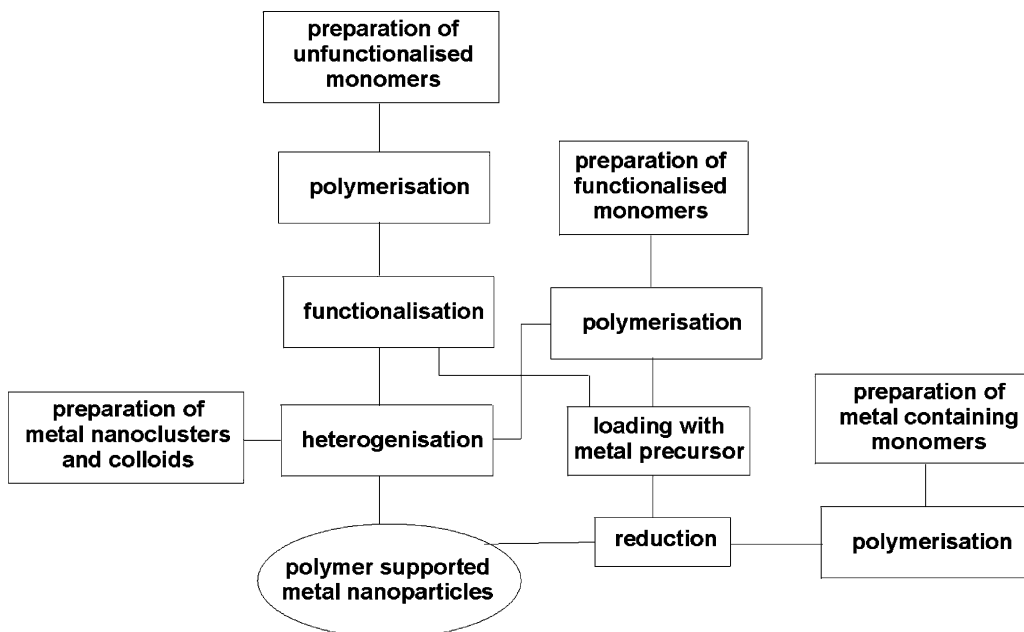


Fig. 1. Routes for the preparation of metal nanoparticles supported on functional polymers.

polymer; (2) loading of the polymer with convenient metal nanoparticle precursors; (3) generation within the polymer of the metal nanoparticles. The first two steps can be condensed in one upon utilisation of metal-containing monomers in the polymer synthesis. Furthermore, the third step can be omitted by directly loading the polymer support with pre-formed metal nanoparticles. The different strategies will be outlined in more detail in the following paragraphs.

Suitable polymer supports can be prepared either by copolymerisation of unfunctionalised monomers followed by functionalisation of the polymer backbone or, more directly, by copolymerisation of functional monomers. The choice of the nature and amount of functional groups to be built in the polymer is made on the basis of the role that they have to play. Their primary function is to bind metal ions or complexes, which are the most common precursors of the metal nanoparticles. Therefore, the kind of functionality which is most usually built in the polymer support is either an ionic moiety (anionic, e.g. sulphonate or carboxylate or cationic, e.g. tetraalkylammonium) whose counter-ion can be readily exchanged, or a group able to co-ordinate to metal centres (e.g. amino or phosphino). Additionally, since the functional groups determine the compatibility of the polymer support with different reagents and solvents (a parameter of chief importance for catalyst performance, as it was discussed in Section 1), they have to be chosen according to the requirements of the particular reaction under study [19,21]. Finally, the functional groups can be also selected in order to influence the catalytic performance of the embedded metal nanoparticles by directly interacting with the metal surface, a phenomenon which was already observed, but which still awaits thorough investigation and rationalisation [11,22].

In order to prepare insoluble resin supports, a certain amount of a suitable cross-linking agent, i.e. a molecule with more than one polymerisable group such as divinylbenzene (DVB), ethylene dimethacrylate, or *N,N'*-methylene-bis(acrylamide), is usually added to the monomer mixture. Thus, in the course of the polymerisation, the different polymerisable groups of the cross-linker are incorporated in different polymer chains, yielding an insoluble polymer network as the reaction product. The amount of cross-linking agent needs to be carefully controlled, since it has a

profound influence on the morphology of the resulting resin. Depending on the cross-linking degree (but not exclusively on this parameter), macroporous (or macroreticular) or microporous (or gel-type) functional resins can be prepared [23]. In the dry state, gel-type resins do not possess any porosity, but they develop an extensive nanometer scale “porosity” (hereafter referred to as nanoporosity) in the swollen state. On the contrary, macroporous resins do possess a permanent micrometer scale porosity even in the dry state (hereafter referred to as macroporosity). Macroporous resins also undergo swelling, albeit to a much lower extent than gel-type ones, and in doing so they develop nanoporosity in addition to the permanent macroporosity. The latter remains largely unaffected by the swelling process. A deeper discussion of this topic and, more generally, of the different experimental techniques which can be employed to prepare resin supports is beyond the scope of this review. The interested reader is referred to other excellent articles and books more fully dedicated to the subject [19,21,23,24].

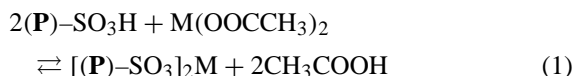
Commercial catalysts are mostly prepared starting from unfunctionalised monomers. Usually, PSDVB resins are formed in the first stage, which are subsequently either sulfonated or chloromethylated and aminated with a tertiary amine resulting in the formation of tetraalkylammonium groups [19]. The route starting from functionalised monomers is exploited to a smaller extent, due to the higher costs of functional monomers. For example, resins which contain carboxylic groups, resulting from the copolymerisation of methacrylic acid (MA) can be conveniently prepared. An advantage of this approach is the much more precise control of the degree of polymer functionalisation, which is especially valuable when a relatively low concentration of functional groups is desired. To achieve this, however, proper polymerisation conditions need to be applied in order to ensure a homogeneous distribution of functional groups throughout the polymer mass [24].

The route starting from metal-containing monomers [25] (the right hand part of Fig. 1) is seldom exploited, for instance when catalysts with peculiar properties are desired. A nice example is a Pd-catalyst prepared from a copolymer of *N,N*-dimethylacrylamide with *N,N'*-methylene-bis(acrylamide) and bis(3-isocyanopropylacrylate)-dichloropalladium(II) by reduction

of the metal with sodium borohydride. This catalyst proved to be particularly stable in the hydrogenation of aromatic nitrocompounds [26].

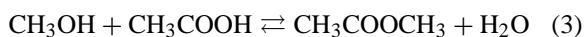
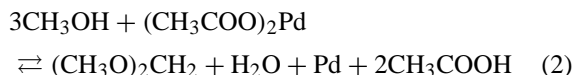
Another possibility deals with the utilisation of metal salts of polymerisable acids such as acrylates or fumarates [27]. The metal-containing monomer can be also formed in situ in the polymerisation mixture. This strategy has been coupled with metal reduction in the course of the polymerisation to yield resin-supported metal nanoparticles from functional monomers, a cross-linker and a metal precursor in one step [28]. It is also possible to generate a layer of a reactive monomer with simultaneous deposition of metal nanoparticles and subsequent fixation of these nanoparticles by polymerisation, as reported by Zavjalov et al. [29], who used [2,2]paracyclophan and palladium nanoparticles generated by an electric arc. At low pressure ( $10^{-7}$  Torr) and temperature (77 K), they deposited this mixture on a silica layer, and after heating to room temperature, a polymerisation resulting in the formation of a poly(*p*-xylene) film occurred, in which the Pd nanoparticles were embedded.

In most cases, the metal is introduced in the pre-formed polymer support by reaction of the polymer-bound functionalities with suitable metal precursors. The metal precursors are easily accessible metal ions or complexes which can be subsequently and conveniently reduced to the form of polymer-supported metal nanoparticles. For example, metal cations can be introduced by simple ion-exchange if pendant anionic groups are present. In this connection, the “forced” ion-exchange technique with metal acetates appears to be a very efficient tool [30]. Here, the metal cations are incorporated in high yields into a resin bearing an excess of strongly acidic groups (most frequently  $-\text{SO}_3\text{H}$  groups). The lower acidity of the acetic acid by-product as well as its volatility enable the reaction to be rapidly driven to completion (Eq. (1); (**P**) and **M** denote the polymer backbone and a divalent metal, respectively):



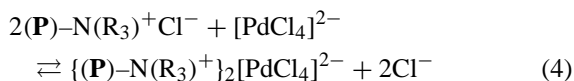
For example, almost quantitative incorporation into an acidic support of both palladium and copper available as acetates in solution was accomplished by “forced” ion-exchange during the preparation of

bimetallic catalysts [31]. A shortcoming of this technique is the possible reduction of a portion of metal if some reducing solvent, e.g. methanol or generally alcohols, is used, according to the following reaction scheme proposed by Yen and Chou [32]:



On the other hand, this phenomenon can be exploited for the direct generation of metal nanoparticles. The reduction of Pd(II) to Pd(0) is easily monitored by a change in colour of a resin from white (yellow, yellowish-brown) to dark brown, or even to black depending of loading of metals [33].

In the case of cationic resins, metallation with cationic species is possible only to a very little extent due to the electrostatic field developed by the pendant cationic groups. Utilisation of proper anionic complexes, like, e.g. chlorocomplexes represents a convenient solution [34].



To ensure the stability of the chlorocomplexes, ion-exchange is carried out in chloride solution; the extent of metal incorporation is about 60–70%.

It is important to remark that a proper choice of the reaction medium for the metal loading reaction is fundamental, especially when resins are used as polymer supports. Thus, a solvent must be chosen which is able to solubilise the metal precursor, but which is also capable of swelling the resin to an appreciable extent, since swelling is needed in order to guarantee the accessibility to the reactants of the majority of the functional groups. The reactivity of the solvent, as in the case mentioned above, needs also to be taken into account.

The final step in the preparation of polymer-supported metal nanoparticles is the generation of the nanoparticles within the polymer, which is usually accomplished by reduction of the polymer-bound metal precursors. To this purpose, similar techniques as in the preparation of conventional metal catalysts supported on inorganic solids may be employed.

However, the lower thermal stability of resin-based catalysts, as well as the already mentioned necessity to swell the resin support in order to guarantee the accessibility of the metal have to be taken into account. The latter factor requires that the reduction is carried out in a liquid-phase, predominantly formed by a solvent with the proper compatibility. The most frequently employed reducing agents are hydrogen, sodium borohydride, hydrazine, alcohols and formaldehyde. When resin supports are employed, their peculiar structure in comparison to traditional inorganic supports determines one of the most interesting properties of these materials. Thus, the growth of the metal nanoparticles during reduction becomes limited by the steric restrictions imposed by the three-dimensional polymer network (Fig. 2), a possibility which permits a certain degree of control on the nanoparticle size [35]. This nanoscale-size controlled generation of metal particles is a challenge to formulation of metal colloid particles, which requires more sophisticated metal precursors, colloid stabilisers and preparation protocols [1,36,37].

The size and size distribution of metal nanoparticles throughout the particles of the support can also depend on other parameters such as the nature and concentration of the reducing agent, the reduction procedure and the metal concentration. We have observed

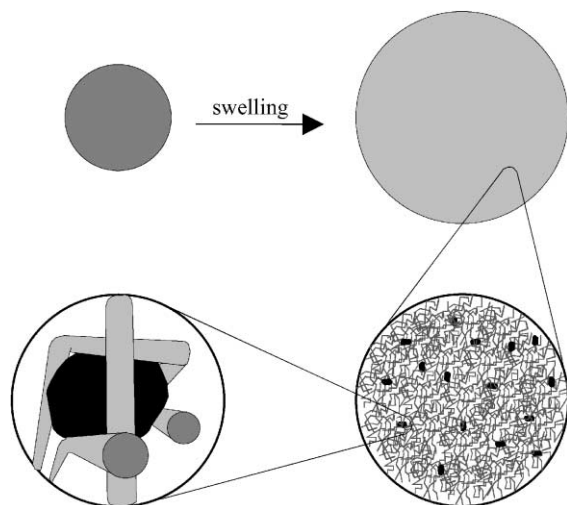
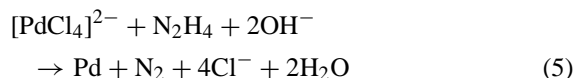


Fig. 2. Sketch showing how the dispersion of Pd(II) inside gel-type resins followed by chemical reduction to metal may lead to the size-controlled growth of Pd nanoparticles.

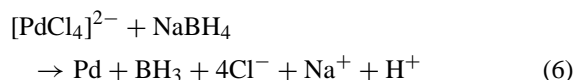
increasing homogeneity of the metal distribution with decreasing metal concentration and increasing concentration of the reductant [33]. This is an interesting feature, since in some cases resin-supported metal catalysts with an inhomogeneous, although controlled, metal distribution throughout the support show superior performance, as in the catalysts for the removal of oxygen from water [16].

A special situation may occur when the polymer-bound metal moiety is difficult to reduce. For example, this is the case of anionic chlorocomplexes present inside a cationic resin. Their reduction requires ligand dissociation in a neutral or basic environment followed by reduction of the metal ion. The reduction can be performed with the following:

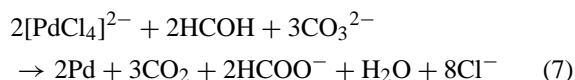
hydrazine:



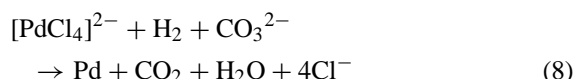
sodium borohydride:



formaldehyde in the presence of carbonates:



Use of a more strongly basic environment provided by hydroxides or carbonates also enables to use dihydrogen as a reduction agent:



However, in all the above-mentioned reactions, the intermediate formation of palladium oxides or hydroxides can complicate the picture, especially for what it concerns the dependence on the reduction conditions of the size of the resulting metal nanoparticles as well as their distribution throughout the catalyst particle [38].

Soluble, polymer-protected metal nanoparticles can be prepared by chemical or electrochemical reduction of solution containing metal precursors as well as soluble polymers ([5], see footnote 1). Block copolymer micelles [39] or microgels [8–10]

containing metal ions can also be conveniently reduced to yield soluble metal nanoparticles. Furthermore, metal nanoparticles prepared by physical means such as metal vapour synthesis [40] can be stabilised with polymer in a second step, thus, yielding again the desired products [41]. The protective polymers are usually functional macromolecules able to give weak interactions with the metal nanoparticle surface, thus, building a protective “shell” of polymer chains. The most commonly encountered polymers are commercial poly-vinylpyrrolidone (PVP), poly-ethyleneimine (PEI) and poly-vinylalcohol (PVA). Such polymer-protected metal nanoparticles can be directly utilised as soluble catalysts or can also be conveniently heterogenised on resin supports by covalent linkage or ligand co-ordination [42]. Alternatively, a resin-grafted protective linear polymer can be used in the metal nanoparticles synthesis, thus, yielding in one step the resin-grafted metal nanoparticles; a nice example of this procedure has been recently described by Chen et al. [11]. An even simpler method for the heterogenisation on functional resins of soluble polymer- and also ligand-stabilised metal nanoparticles is the simple absorption of the metal nanoparticles inside the functional resin [43]. A rather high degree of swelling of the resin and/or the presence of macropores is needed in order to guarantee the accessibility of the resin network to the metal nanoparticles. The stabilising polymer or ligands can be removed from the metal surface in a second step, thus, yielding resin-supported, “naked” metal nanoparticles. This procedure obviously implies higher costs and complexity in comparison to the generation of metal nanoparticles from resin-bound metal precursor. On the other hand, these strategies often allow a higher degree of control on the metal nanoparticle size and especially on the size distribution.

### 3. Characterisation of metal catalysts supported on functional polymers

The characterisation of a complex system such as a supported metal catalyst can be thoroughly accomplished only by using numerous different techniques. Basically, the properties which need to be evaluated can be divided into two groups: (i) properties of the support, such as its grain size, morphology, porosity,

chemical composition, kind and degree of functionalisation, degree of hydrophilicity/hydrophobicity, etc.; (ii) properties of the supported metal particles, such as their size and size distribution, degree of crystallinity, presence of defects, distribution throughout the support grains, etc. All these properties may more or less contribute to the overall catalytic activity of the supported catalyst.

Many different methodologies have been developed over the years for the characterisation of resin supports. A comprehensive account on this topic is given in another chapter of this issue [44]. On the other hand, the techniques employed for the characterisation of metal particles supported on functional polymers are in most cases similar to those exploited for inorganic based catalysts, e.g. chemical analysis, evaluation of metal surface area by adsorption–desorption isotherms, determination of metal particle size and degree of crystallinity by electron microscopy, etc. [45]. A recent brief and comprehensive description of TEM, UV–VIS, IR, X-ray and NMR methods for characterisation of colloidal metal particles has been presented by Toshima and Yonezawa [46]. However, the application of some of these techniques to a material with rather peculiar properties such as a resin-supported metal catalyst deserves a few additional comment. For example, the exploitation of methods like X-ray powder diffraction (XRPD) analysis, electron spectroscopy for chemical analysis (ESCA), and X-ray microprobe analysis (XRMA) is simpler because of the amorphous state of the usual resin supports; on the other side, the application of mercury porosimetry is restricted for resin-based catalysts due to their low mechanical stability; electron spectroscopy is complicated by the low electric conductivity of the organic support, etc.

The average size of metal crystallites can be simply estimated by means of XRPD [46,47]. However, the determination of this quantity for catalysts containing <0.5 wt.% of metal, or in the case of very small metal particles (<2 nm large) is very biased due to the low intensity of the diffraction band [47,48]. In the cases of small metal crystallites and/or low metal content, the size of the metal particles may be determined more precisely by transmission electron microscopy (TEM).

Recently, more sophisticated techniques have been applied to the characterisation of metal catalysts supported on functional polymers, of which the extended

X-ray absorption fine structure (EXAFS) is of growing importance. For example, Lin et al. [49] have described changes in the average size of palladium nanoparticles deposited on PSDVB beads with a BET surface area of  $465 \text{ m}^2/\text{g}$  (prepared by impregnation with tetraaminopalladium(II) chloride, evaporation of water, drying and reduction with hydrogen at  $200^\circ\text{C}$ ) after having been used as oxidation catalysts. It has been revealed from EXAFS spectra that the co-ordination number of palladium in the nanoparticles increased from 3 in the original catalyst up to 7.9; correspondingly, the average diameter of the nanoparticles was found to vary from 0.6 to 2 nm, before and after catalytic tests.

The characterisation of dispersed metals by sorption methods usually fails in the case of metal dispersed onto functional polymers due to the poor accessibility of the metal nanoparticles which are usually more or less buried inside the polymer network, and are therefore, accessible only after proper swelling of the polymer network. This phenomenon was demonstrated also for macroporous resin supports, such as the commercial Bayer acidic resin UCP 118 [50]. The resin was loaded with 2 wt.% of Pd by ion-exchange and subsequent reduction. The metal was found to be located in a polymer layer at the surface of the resin macropores. Since the resulting metal particles were embedded in this layer, they turned out to be inaccessible to simple gaseous reactants such as carbon monoxide.

An assessment of the catalytic potentiality of resin-based metal catalysts designed for reactions in liquid and/or vapour phase can be performed using titration methods in a solvent compatible with the resin. Kljuev and Nasibulin [51] showed that 0.2 mol of mercury acetate per 1 mol of Pd totally killed catalytic activity of the Pd/APSDVB for the hydrogenation of nitrobenzene. Titration with thiophene (TF) showed a similar tendency as that with mercury acetate, but a low catalytic activity remained even after addition of a relatively large amount of TF: indeed, even at a molar ratio  $\text{TF}/\text{Pd} = 1$ , the catalyst exhibited residual activity.

Finally, it must be remarked that a full description of the behaviour of a metal catalyst supported on functional polymers requires a thorough investigation on the transport phenomena inside the polymer support, which often govern the productivity of the

catalyst. In this connection, we have succeeded in developing a mathematical model able to correlate some structural features of the polymer-supported metal catalyst, such as the accessibility of the polymer support or the average size of the metal particles, with the overall catalyst activity in a model reaction [52,53]. It is our feeling that more investigations of this kind are needed in order to come to a rational understanding of the influence of the various structural parameters on the overall catalyst performance.

#### 4. Applications of metal catalysts supported on functional polymers

In this chapter, selected catalytic processes carried out over polymer-supported metal catalysts are discussed in more detail. If there is available information, a comparison with catalysts based on more traditional inorganic supports is reported. A few cases dealing with stabilised colloids and metal complexes supported on resins are also included for sake of comparison.

##### 4.1. Hydrogenation processes

###### 4.1.1. C:C bonds

The hydrogenation of C:C double and triple bonds is a very common reaction in heterogeneous metal catalysis. The numerous reported examples can be classified into a few reaction types: (i) total hydrogenation of an unsaturated molecule without other hydrogenatable moieties; (ii) partial hydrogenation of a molecule with more than one multiple bond, either conjugated or not; (iii) partial hydrogenation of alkynes to alkenes; (iv) selective hydrogenation of an unsaturated molecule bearing other hydrogenatable moieties, such as carbonyl groups or halogen substituents.

The total hydrogenation of C:C bonds over inorganic catalysts is a well established technology, the most important industrial application probably being the hydrogenation of benzene to cyclohexane [17]. Concerning metal catalysts supported on functional polymers, the total hydrogenation of unsaturated molecules has been mainly used as a model reaction for the estimation of the catalytic activity [11,22,33,34,47,48,54], as well as for the evaluation of both the



intrinsic reaction kinetics and transport phenomena within the polymer support [52,53].

Chen et al. [11] have reported about very active and stable platinum colloidal catalysts prepared by alcohol reduction of  $\text{PtCl}_6^{2-}$  using poly(*N*-isopropylacrylamide) previously grafted on PS microspheres as stabilising polymer. The observed catalytic activity in the hydrogenation of allyl alcohol was more than five times higher than with Pt/C. Moreover, it was possible to recycle the resin-based catalysts for at least six times, whereas Pt/C was not recyclable at all. When comparing the catalytic activity of free and heterogenised colloidal platinum particles, only a little decrease in the reaction rate was observed (see Table 1).

Sabadie and Germain [55] investigated the stereoselectivity of polymer-supported metal catalysts in the hydrogenation of 1,2-dimethylcyclohexene. Depending on the pressure of hydrogen, different

ratios of *cis*- and *trans*-isomers (0.44 and 0.57 at 1.25 and 10 MPa, respectively) of 1,2-dimethylcyclohexanes were obtained over Pd/APSDVB catalysts.

The partial hydrogenation of dienes was successfully carried out by Michalska et al. [56] using palladium supported on heterocyclic polyamides. Under the reaction conditions employed (MeOH, atmospheric pressure, 25°C) the resin-supported catalyst was able to selectively hydrogenate one of the two double bonds present (Table 2). Recycling experiments proved the high stability of the used catalysts. For example, in 11 hydrogenation runs with 2-methyl-1,3-pentadiene, which is equivalent to 4300 catalytic cycles per palladium atom, neither loss of activity nor changes in selectivity were observed.

A successful partial hydrogenation of alkynes to alkenes in the presence of other double bonds in the substrate was also reported by Sulman et al. [57] who prepared linalool (LN, 3,7-dimethyl-1,6-octadiene-3-

Table 1

Turnover frequency (TOF) in the hydrogenation of various substrates with a multiple C:C bond

Reference	Catalyst/solvent	Substrate	<i>P</i> (bar)	<i>T</i> (°C)	Recycling	TOF (mol <sub>H<sub>2</sub></sub> / (mol <sub>M</sub> min))
[42]	Pt/{poly-[ <i>N</i> -(2-aminoethyl)acrylamide]-co-[(4-nitrophenyl) acrylate]-co-[( <i>N</i> -vinyl)pyrrolidone]}/EtOH:water = 1:1	CH <sub>3</sub> CH <sub>2</sub> OCH=CH <sub>2</sub>	1	30	0	9.6
		Cyclohexene	1	30	0	2.2
		Acrylonitrile	1	30	0	1.3
	Colloidal Pt/{poly-[(4-nitrophenyl)acrylate]-co-[( <i>N</i> -vinyl)pyrrolidone]}/EtOH:water = 1:1	CH <sub>3</sub> CH <sub>2</sub> OCH=CH <sub>2</sub>	1	30	0	20.4
		Cyclohexene	1	30	0	14.4
		Acrylonitrile	1	30	0	2.7
	5% Pt/C/EtOH:water = 1:1	CH <sub>3</sub> CH <sub>2</sub> OCH=CH <sub>2</sub>	1	30	0	0.01
		Cyclohexene	1	30	0	0.13
		Acrylonitrile	1	30	0	0
[11]	Pt/{poly-styrene-co-( <i>N</i> -isopropyl)acrylamide)}/water	CH <sub>2</sub> =CHCH <sub>2</sub> OH	1	25	0	5.1
			1	25	5	4.9
	Pt/{poly-styrene}/water	CH <sub>2</sub> =CHCH <sub>2</sub> OH	1	25	0	3.8
			1	25	5	2.0
	3% Pt/C/water	CH <sub>2</sub> =CHCH <sub>2</sub> OH	1	25	0	1.0
			1	25	1	n.u. <sup>a</sup>
[53]	2% Pd/{poly-{ <i>N,N</i> -dimethyl)acrylamide}-co-{sodium-4-styrylsulphonate}-co-{methylenebis(acrylamide)} P4 and P8, 4 and 8 mol% cross-linked, respectively/MeOH	Cyclohexene (P4)	5	25	0	173
			5	25	3	170
		Cyclohexene (P8)	5	25	0	103
			5	25	3	104

<sup>a</sup> n.u.: not usable.

Table 2

Hydrogenation of dienes and acetylenes from [56] at 1 bar 25°C in MeOH, 2 mM Pd/I

Catalyst	Substrate (mol/l)	TOF (mol <sub>H<sub>2</sub></sub> / (mol <sub>M</sub> min)) <sup>a</sup>	Conversion (%)	Selectivity (%) <sup>b</sup>
$\text{Pd} / \left[ \text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \text{---} \text{C}_5\text{H}_4\text{N} \text{---} \text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \text{---} \text{N}(\text{CH}_2)_6\text{N} \right]_n$	2-Methyl-1,3-pentadiene (1)	67	35	88
	1,4-Cyclohexadiene (1)	100	80	80
	1,7-Octadiene (1)	125	65	65
	Phenylacetylene (0.77)	15	100	100
	2-Hexyne (0.77)	5	100	81
0.1% Pd/C	2-Methyl-1,3-pentadiene (1)	5.5	100	0
	Phenylacetylene (0.77)	22	100	0
	2-Hexyne (0.77)	26	100	0

<sup>a</sup> Calculated from the time at 100% conversion of diene supposing the total hydrogenation.<sup>b</sup> Selectivity to unsaturated product.

ol) by the selective hydrogenation of dehydrolinalool (DHL, 3,7-dimethyl-octa-6-ene-1-yne-3-ol) using a Pd/PVP/Al<sub>2</sub>O<sub>3</sub> catalyst. They achieved 99.8% selectivity to LN in toluene at 90°C and 0.1 MPa by running the reaction under hydrogen limitation (480 min<sup>-1</sup> reactor shaking frequency). The catalyst was recycled for 20 times and exhibited higher stability than an analogous catalyst prepared from a polystyrene-co-butadiene copolymer deposited on Al<sub>2</sub>O<sub>3</sub>.

Recently, we have reported [22] about the role of the solvent in the determination of the catalytic performance of resin-supported palladium catalysts in the hydrogenation of alkenes. Substrates with

different lipophilicity (cyclohexene, cyclohexanone, 2-cyclohexene-1-one) often interact to a different extent with the polymer chains of the swollen polymer network, which results in different barriers to diffusion throughout the support. We have found that such interactions between substrate and polymer backbone can be suppressed by utilising a reaction solvent which itself strongly interacts with the polymer chains (in this case MeOH). Use of methanol as reaction medium resulted in a comparable hydrogenation rate of both cyclohexene and 2-cyclohexene-1-one. Furthermore, a strong promoting effect on the reaction rate by pendant amide groups was recorded (Fig. 3).

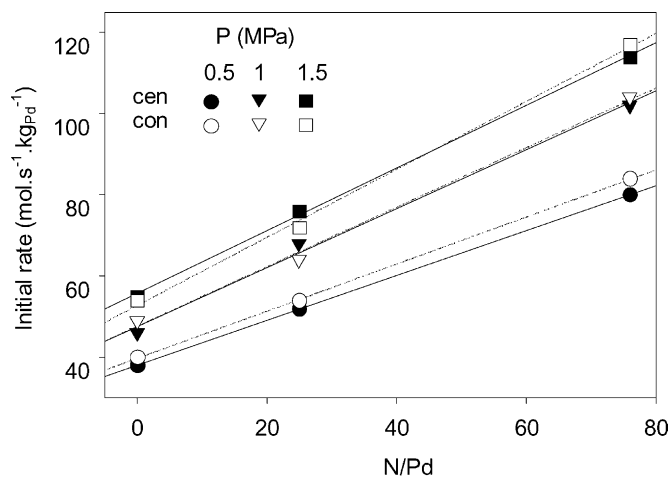


Fig. 3. Initial hydrogenation rate of cyclohexene (cen) and 2-cyclohexene-1-one (con) over catalysts with different (N/Pd) molar ratios. Various molar ratios of N/Pd were achieved upon polymerisation of different molar fractions of monomers (*N,N*-dimethylacrylamide; 2-methacryloylsulphonic acid; styrene; *N,N'*-methylene-bis(acrylamide); divinylbenzene). Details about polymerisation and preparation of catalysts are in [26].

Table 3

Hydrogenation of benzene over various metal-supported catalysts

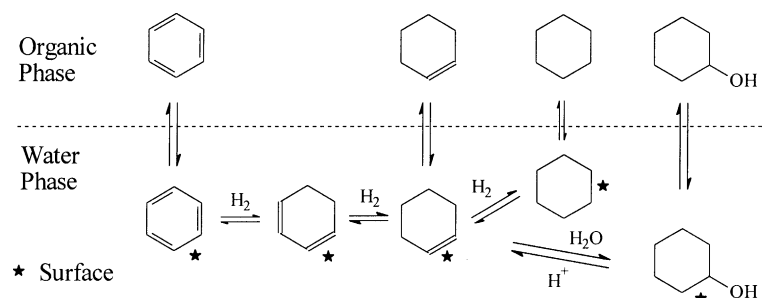
Reference	Catalytic system	Phase <sup>a</sup>	<i>P</i> (MPa)	<i>T</i> (°C)	<i>X</i> (%) <sup>b</sup>	<i>S</i> (%) <sup>c</sup>
[59]	0.6% Pt/{Nylon-6}	(G + V)–S	0.1	140	5.2	7.3
		(G + V)–S	0.1	160	6.0	8.8
	6.6% Pt/{Amberlite IR 120} <sup>d</sup>	(G + V)–S	0.1	140–190	0	–
	4.5% Pt/{Amberlite CG 400} <sup>e</sup>	(G + V)–S	0.1	140–190	0.1–0.3	0
	0.05% Pt/Al <sub>2</sub> O <sub>3</sub>	(G + V)–S	0.1	160	1.6	0
[60]	1% Pd/{Nylon-6}	(G + V)–S	0.1	150	1	3
	1% Pt/{Nylon-6}	(G + V)–S	0.1	150	2	17
	1% Rh/{Nylon-6}	(G + V)–S	0.1	150	1.8	50
[61,62]	Colloidal Ru/{water + ZnSO <sub>4</sub> }/organic phase	(G + V)–L–L–S	5	150	54	51.3
	Colloidal Ru/water/organic phase	(G + V)–L–L–S	5	150	38	1.3
[63]	4% Ru/M <sup>f</sup> /water/organic phase	(G + V)–L–L–S	1.5	100	47	8.1
	4% Ru/P <sup>g</sup> /water/organic phase	(G + V)–L–L–S	1.5	100	46	5.6
	4% Ru/S <sup>h</sup> /water/organic phase	(G + V)–L–L–S	1.5	100	43	3
	4% Ru/P <sup>g</sup> /organic phase	(G + V)–L–S	1.5	100	4.3	9.3
[64]	0.25% Ru/{H <sup>+</sup> -mordenite}/water/organic phase	(G + V)–L–L–S	5	150	40	83 <sup>i</sup>
			5	200	65	53 <sup>i</sup>

<sup>a</sup> G, V, L, S are gas, vapour, liquid and solid phases, respectively.<sup>b</sup> Conversion of benzene.<sup>c</sup> Molar selectivity to cyclohexene.<sup>d</sup> Strongly acidic microporous SPSDVB; 8 mol% cross-linked.<sup>e</sup> Strongly basic microporous APSDVB.<sup>f</sup> Poly-(*N,N*-dimethylacrylamide)-co-(potassium 1-methacryloyl ethylene-2-sulphonate)-co-(*N,N'*-methylene-bis(acrylamide)); 4 mol% cross-linked.<sup>g</sup> Poly-(*N,N*-dimethylacrylamide)-co-(sodium styrene-4-sulphonate)-co-(*N,N'*-methylene-bis(acrylamide)); 4 mol% cross-linked.<sup>h</sup> SPSDVB; 4 mol% cross-linked.<sup>i</sup> The sum of selectivities to cyclohexene and cyclohexanol.

The production of cyclohexene by partial hydrogenation of benzene is a reaction of great theoretical and industrial interest [58]. Dini et al. [59] prepared various platinum catalysts by impregnation and ion-exchange on different supports such as Nylon-3 (prepared from acrylamide using NaNH<sub>2</sub> as a catalyst), Nylon-6, poly-acrylamide, poly-acrylamideoxime, poly-acrylonitrile, pyro-poly-acrylonitrile and poly-*p*-phenyleneterephthalamide, commercially available SPSDVB resins (DOWEX 50 W and Amberlite CG 400), zeolite NaY and  $\gamma$ -alumina. The reduction of Pt(II) to Pt(0) was carried out with hydrogen prior to catalyst use. The gas phase hydrogenation of benzene, performed in a fixed-bed reactor at atmospheric pressure and temperature 140–190°C keeping the stoichiometric molar ratio dihydrogen:benzene = 3, showed Pt/Nylon-6 to be the most selective catalyst. However, selectivity for cyclohexene was found to decrease strongly with increasing benzene conversion.

Table 3 contains a few results obtained by these authors.

A similar behaviour of Pt/nylon catalysts was observed by Galvagno et al. [60] who tested palladium, platinum and rhodium deposited on Nylon-66 beads (50–100 mesh). The Rh/nylon catalyst turned out to be the most selective (Table 3); at 3% conversion of benzene, about 40% selectivity was achieved (fixed-bed reactor, atmospheric pressure, 150°C, H<sub>2</sub>:C<sub>6</sub>H<sub>6</sub> = 3), while palladium and platinum catalysts exhibited only about 1–10% selectivity, respectively. The higher selectivity of rhodium catalysts can be explained by the weak chemisorption of both benzene and hydrogen on the rhodium surface. In fact, the weak chemisorption of the benzene molecule on rhodium implies a preferentially perpendicular orientation of chemisorbed benzene in respect to the metal surface. Consequently, one “double bond” from the conjugated  $\pi$ -system is predominantly hydrogenated



Scheme 1. Biphasic stepwise hydrogenation of benzene.

in the initial stages of the reaction, and the other two are attacked only in a second step. On the other hand, the stronger chemisorption of hydrogen on palladium and platinum favours the total hydrogenation of benzene to cyclohexane. Even higher selectivity was obtained over a Rh/nylon catalyst pre-treated in air, which confirms the hypothesis about the positive influence on reaction selectivity of a decrease in the chemisorption strength of the reactants.

We have attempted to apply this principle for the development of tailored resin-supported metal catalysts for the partial hydrogenation of benzene. Our idea was to embed the metal catalyst in a hydrophilic resin support able to retain water while carrying out the reaction in benzene, thus creating a sort of “water-in-oil” biphasic system (Scheme 1). The hydrophilic environment around the metal particles should help decreasing benzene chemisorption as proved by Struijk et al. [61,62]. The hydrogenation was carried out over ruthenium catalysts, which are cheaper than rhodium ones. We have utilised [63] ruthenium catalysts deposited on functional resins with different hydrophilicity either 4 or 8 mol% cross-linked. The catalysts were prepared by ion-exchange with hexaaminoruthenium(II) chloride and reduced with sodium borohydride. A uniform distribution of about 3 nm large metal crystallites (estimated from XRPD measurements) throughout the catalyst particles was obtained, as shown by XRMA. Fig. 4 and the data in Table 3 illustrate the importance of a hydrophilic microenvironment provided by the polymer support around the ruthenium-crystallites. In addition, higher flexibility and lower bulkiness of the  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{SO}_3^-$  in the comparison with  $-\text{Ph}-\text{SO}_3^-$  groups enabled a higher reaction rate and higher selectivity

in the case of Ru/M catalyst than it was over Ru/P catalyst. Lowering in the reaction rate is also caused by a higher affinity of benzene ring to the phenylene part of the polymer structure. A similar situation has been also observed in the hydrogenation of 2-ethyl-antraquinone (2-EtAQ).

Unfortunately, the thermal and chemical stability of these supported catalysts is not sufficient to sustain the more drastic reaction conditions (5 MPa, 150°C) required for shortening the reaction time and rendering the reaction suitable for technological purposes. However, this investigation helped us to develop a process for the partial hydrogenation of benzene coupled with the hydration of the formed cyclohexene over ruthenium deposited on inorganic hydrophilic materials (the last two rows in Table 3) [64].

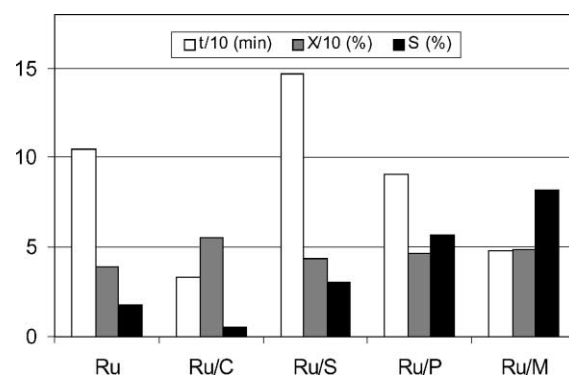


Fig. 4. Hydrogenation of benzene to cyclohexene over various ruthenium catalysts at 1.5 MPa, 110°C, 2 ml benzene, 0.75 ml water, 2 mg Ru in the catalyst. Reaction time ( $t$ ), conversion of benzene ( $X$ ) and selectivity of cyclohexene formation ( $S$ ). M — methacryloyl, P — dimethylacrylamide and S — sulfonated poly-styrene based catalysts [63].

A modern reactor build-up for hydrogenation reactions represented by polymeric membrane reactors has been intensively investigated by Gao and co-workers [65–69]. The membrane catalysts were prepared by pumping an aqueous solution of palladium dichloride through a membrane formed by a functional polymer, e.g. PVP, melamine-formaldehyde resin, poly-acrylonitrile, or cellulose acetate (CA). Hydrazine or sodium borohydride were then used to reduce Pd(II) to Pd(0). Under hydrogenation conditions (atmospheric pressure and temperature up to 40°C) the prepared catalysts were stable, active and selective in the hydrogenation of dienes and alkynes. For example, in the treatment of a propene fraction about 97% conversion of existing propyne and propadiene (allene) impurities was achieved at only little hydrogenation of propene to propane. A remarkable synergic effect of PVP and CA admixtures was reported in the hydrogenation of crude 1-butene containing 0.6% of butadiene over the Pd/(PVP-CA) catalyst. A complete conversion of butadiene was observed, but about 2.6% of 2-butene formed. However, using Pd-Co supported on a PVP-CA membrane the isomerisation was suppressed. A selective hydrogenation of cyclopentadiene to cyclopentene was also performed with excellent results using this catalyst.

#### 4.1.2. C:O bonds

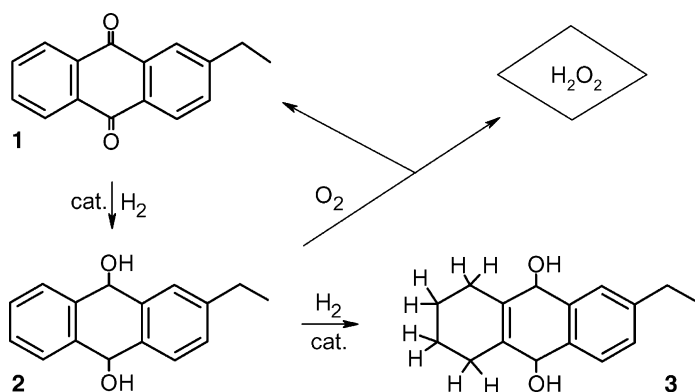
A very important industrial process involving the hydrogenation of C:O double bonds is the production of hydrogen peroxide by the anthraquinone method. In this technology, 2-ethylanthraquinone is hydro-

genated over Pd metal catalysts to the corresponding hydroquinone (compound **2** in Scheme 2). Subsequent re-oxidation of the hydroquinone product by air generates hydrogen peroxide [70].

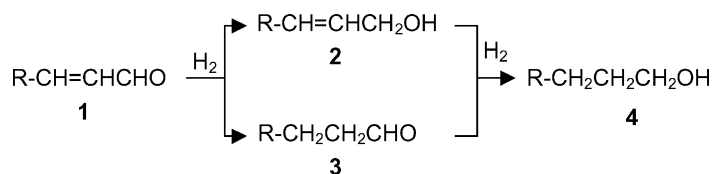
The main drawback of this reaction is represented by the anthraquinone losses which originate from different side reaction, the most important of which is ring hydrogenation yielding tetrahydroanthraquinone (the product **3** in Scheme 2) and eventually octahydroanthraquinone, which cannot be re-oxidised.

Drelinkiewicz et al. [38,71] have thoroughly investigated the use of Pd supported on nitrogen containing polymers such as poly-4-vinylpyridine and poly-aniline. They have established useful correlation between the procedure employed for loading the metal precursor on the polymer support, the resulting metal speciation in the polymer and the size and size distribution of the Pd particles obtained after metal reduction. However, the resulting catalysts were neither particularly active nor very selective for the hydroquinone product.

On the basis of knowledge, stemming from our laboratories, we have devised a few very lipophilic functional resins aimed at supporting 3–4 nm Pd nanoclusters. The idea was to promote in this way the desorption from the catalyst particles of the hydrophilic hydroquinone product, thus, preserving it from further ring hydrogenation. Upon playing with the primary structure of the polymer backbone and with the nature of the reaction medium, we have succeeded in promoting a chemoselectivity to 2-ethylanthrahydroquinone equal to 96%, i.e. slightly, but definitely superior to



Scheme 2. The anthraquinone production route of hydrogen peroxide.



Scheme 3. Hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes; R represented by Ph and CH<sub>3</sub> denote cinnamaldehyde and 2-butenal, respectively.

that provided by a commonly employed commercial catalyst under identical conditions, while maintaining a comparable level of catalytic activity [72,73]. Better results were obtained with supports containing polymer chains with long alkyl substituents in comparison with phenyl substituents [73].

The selective hydrogenation of the carbonyl group of  $\alpha,\beta$ -unsaturated aldehydes (Scheme 3) has been the aim of the research of Yu et al. [43] who have prepared various platinum and palladium catalysts supported either on inorganic supports ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>,) or organic resins (macroporous PS beads). Metal colloids were prepared by alcohol reduction in the presence of PVP as stabiliser. The obtained nanoclusters (about 1.1 nm average size) were deposited by stirring a solution containing the metal-PVP colloids with the support for 24 h at ambient temperature. Extraction with an EtOH–H<sub>2</sub>O mixture removed PVP, leaving the “naked” metal nanoparticles on the support. The reported selectivity to COL for the PS supported catalyst is comparable with that obtained over the best inorganic catalyst (Table 4), but the reaction rate was higher by approximately 50%; furthermore, the catalytic activity of a recycled Pt/PS catalyst was the same as that of original one, thus, suggesting good catalyst stability under the reaction conditions employed.

Under similar conditions, Yu et al. [74] investigated effects of added transition metals salts on the selective hydrogenation of CAL to COL and of 2-butenal to 2-butenol. In both cases, the selectivity for the unsaturated alcohols was significantly increased by the addition of transition metals, especially iron and cobalt. Due to steric effects (the size of a methyl group is smaller than that of a phenyl: therefore, the double C:C bond is closer to the metal surface in 2-butenal than in CAL), a higher selectivity was obtained in the hydrogenation of CAL than in that of 2-butenal.

#### 4.1.3. N:O bonds

The metal catalysed hydrogenation and hydrogenolysis of nitro-, nitroso-, azo- and nitrile-groups represents a class of reactions widely employed in industrial organic synthesis [75–77] which are commonly encountered also in large-scale chemical production plants (e.g. in the preparation of aniline from nitrobenzene).

Scheme 4 depicts the main reaction routes in the hydrogenation of nitrobenzenes (**1a**). Substrates with X = hydrogenatable group such as halogen, sulfenamide, alkyl chain with ether or multiple C:C bonds are difficult to hydrogenate selectively [76]. The hydrogenation of hydroxylamine (**3**) proceeds

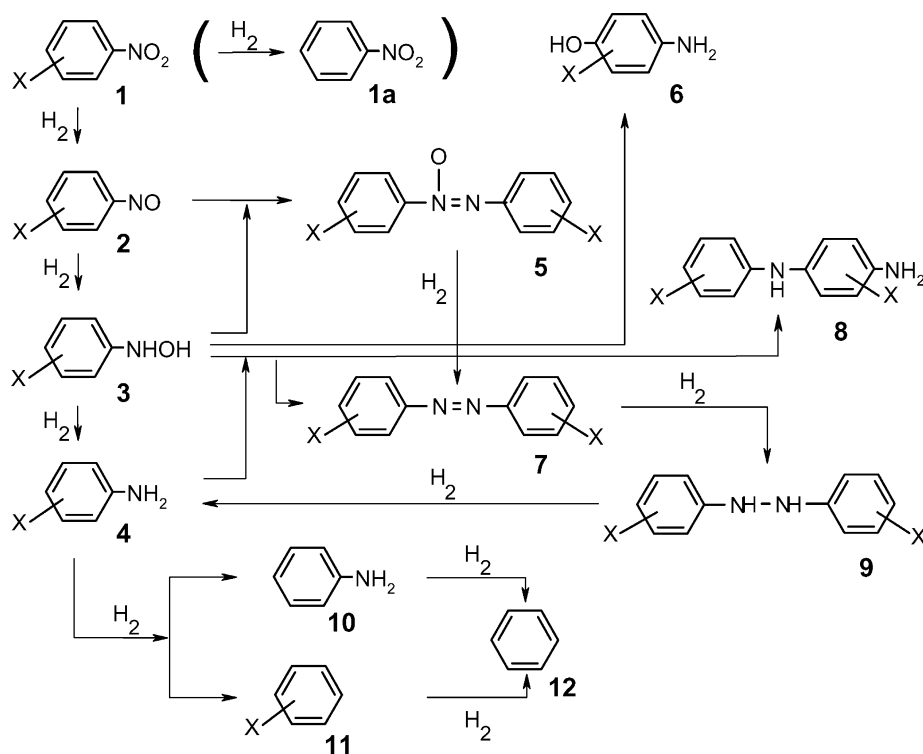
Table 4

Hydrogenation of various  $\alpha,\beta$ -unsaturated aldehydes carried out at 4 MPa and 60°C

Reference	Catalyst	Aldehyde	X (%) <sup>a</sup>	S <sub>1</sub> (%) <sup>b</sup>	S <sub>2</sub> (%) <sup>b</sup>	S <sub>3</sub> (%) <sup>b</sup>
[43]	Colloidal Pt/PVP	PhCH=CHCHO	37.5	12	80	8
	0.5% Pt/PS	PhCH=CHCHO	79.7	94.7	5.7	Trace
	0.5% Pt/MgO	PhCH=CHCHO	61.5	97.1	2.9	Trace
[74]	Colloidal Pt/PVP/ZnCl <sub>2</sub>	PhCH=CHCHO	29.2	99.8	0.2	0
	Colloidal Pt/PVP	CH <sub>3</sub> CH=CHCHO	60.2	10.2	85.3	4.5
	Colloidal Pt/PVP/FeCl <sub>3</sub>	CH <sub>3</sub> CH=CHCHO	70.5	48.9	33.1	18

<sup>a</sup> Conversion of the substrate.

<sup>b</sup> Molar selectivities to unsaturated alcohol (S<sub>1</sub>), saturated aldehyde (S<sub>2</sub>) and saturated alcohol (S<sub>3</sub>).



Scheme 4. Possible reaction pathways in the hydrogenation of aromatic nitrocompounds.

with a good yield over catalysts with low metal loading which do not suffer from significant mass transport hindrances, thus, allowing rapid diffusion from the catalytic sites. The formation of dimeric products of azoxy (**5**) and azobenzene (**7**) type is favoured by a basic reaction environment. The formation of 4-aminophenol (**6**) by the Bamberger's rearrangement route [78] requires a strong acidic medium, e.g. sulphuric acid, and a temperature higher than 80°C. Under proper acidic conditions achieved mainly by addition of hydrochloric acid, the reaction of *N*-phenylhydroxylamine (**3**) with aniline yielding aminodiphenylamines can proceed [79]. Azoxybenzenes (**5**) are easily converted to azobenzenes (**6**) and hydrazobenzenes (**9**) which can be subsequently hydrogenolysed to amines, even at atmospheric pressure [80]. Of course, the latter outlined route also increases the extent of reaction of other hydrogenatable groups X present. The desired amine (**4**) can in principle react further resulting in the cleavage of the substituent X (**10**), of the amino group (**11**), or of

both (**12**). The cleavage of the substituent X can also occur in the course of the formation of nitroso- (**2**) and *N*-hydroxylamino-intermediates. When a selective hydrogenation of nitrogen containing aromatic compounds is desired, special procedures are used, e.g. that for the preparation of aminoazobenzene compounds by selective reduction of the corresponding nitroazobenzenes with hydrazine hydrate [81]. More complicated reactions leading to more highly condensed products are not involved into Scheme 4. However, they need to be considered as factors responsible for lowering the yield of the desired product **4** and for catalyst deactivation by deposition of polymeric by-products on the active sites.

If a sufficiently active catalyst is used, the most probable path for the formation of the amine (**4**) from the corresponding substituted nitrobenzene (**1**) is through nitroso- and *N*-hydroxylamine intermediates; an attack on the substituent X lowers the yield of the product. Abdullajev et al. [80] have shown that over palladium supported on a cationic resin

bearing tetraalkylammonium groups nitrobenzene, *o*-nitrotoluene and *o*-nitro-ethylbenzene are virtually 100% converted to amines at 40°C and 100 kPa of H<sub>2</sub> in ethanol without significant formation of side products.

A few selected data about the hydrogenation of substituted aromatic nitrocompounds with different catalysts are reported in Table 5. They show that metals supported on a resin can exhibit comparable or even higher catalytic activity than inorganic based catalysts.

For the high-yield synthesis of chloroanilines (CAn) from the corresponding chloronitrobenzenes (CNB), deactivated platinum catalysts, or even better iridium

catalysts are used [82]. Simple palladium catalysts are not very selective, e.g. Abdullajev [80] obtained only 40% yield of CAn from the corresponding CNB. Low selectivities were also observed by Yu et al. [83] who reported that the cleavage of chlorine from *p*-CNB was the main reaction consuming *p*-CNB when palladium supported on PVP was used. Aniline is formed in a second step. Much better results were achieved using a PVP-PdCl<sub>2</sub>-MX catalyst with MX = RhCl<sub>3</sub>, or RuCl<sub>3</sub>, whereas the latter was significantly more efficient. About 94% selectivity to *p*-CAn was achieved at virtually total conversion of CNB (0.1 MPa H<sub>2</sub>, 65°C, TOF<sub>max</sub> = 7.7 min<sup>-1</sup>). Yang et al. [84,85]

Table 5

Hydrogenation of substituted nitrobenzenes; data for inorganic catalysts are given for comparison

Reference	Catalyst/solvent	Substrate	<i>P</i> (MPa)	<i>T</i> (°C)	TOF (mol <sub>H<sub>2</sub></sub> / (mol <sub>M</sub> min)) <sup>a</sup>	<i>X</i> (%) <sup>b</sup>	<i>S</i> (%) <sup>c</sup>
[115]	5% Pd/C/MeOH	2,4-Dinitrotoluene	2	35	120 (i) <sup>d</sup>	100	100
[116]	5% Pd/C/EtOH	2,4-Dinitrotoluene	0.1	5	5.3 (i) <sup>e</sup>	100	100
[117]	1% Pd/(AV-17-8) <sup>f</sup> /EtOH	4-Nitrotoluene	0.1	45	0.69 (a) <sup>g</sup>	100	100
[112]	0.5% Pd/S4 <sup>h</sup> /MeOH	4-Nitrotoluene	0.75	30	173 (i) <sup>i</sup>	100	100
[80]	1% Pd/(AV-17-8) <sup>f</sup> /BuOH	2-Nitrotoluene	0.1	20	2.9 (a) <sup>j</sup>	100	100
	1% Pd/(AV-17-8) <sup>f</sup> /EtOH	Azoxybenzene	0.1	40	23.7 (i) <sup>k</sup>	100	100
[118]	1% Pt-S/C/MeOH	3-Chloronitrobenzene	0.66	40	8.6 (i) <sup>l</sup>	100	99.8
[83]	PVP-PdCl <sub>2</sub> -RuCl <sub>3</sub> -NaOAc/MeOH	4-Chloronitrobenzene	0.1	65	10.1 (i) <sup>m</sup>	98	94
[119]	1% Pd/S4 <sup>h</sup> /MeOH + DETE	4-Chloronitrobenzene	0.5	25	20.1 (a) <sup>n</sup>	100	96.5
	1% Pd/C/MeOH + DETE	4-Chloronitrobenzene	0.5	25	9.1 (a) <sup>n</sup>	100	90.5
[106]	1% Pd/S4 <sup>h</sup> /MeOH	4-Nitrophenol	0.5	25	6 (i) <sup>o</sup>	95	100
	1% Pd/C/MeOH	4-Nitrophenol	0.5	25	1.1 (i) <sup>p</sup>	70	100
[96]	3% Pt/C/(10% H <sub>2</sub> SO <sub>4</sub> )	Nitrobenzene	2.72	80	2332 (i) <sup>r</sup>	100	70 <sup>s</sup>
[120]	Pd/PVP/(water + H <sub>2</sub> SO <sub>4</sub> )	Nitrobenzene	0.1	84	1.5 (a) <sup>t</sup>	90	62 <sup>s</sup>

<sup>a</sup> TOF = turnover frequency: (i) initial and (a) average up to stoichiometric consumption of hydrogen supposing the 100% selectivity to corresponding aminoderivative.

<sup>b</sup> Conversion of substrate.

<sup>c</sup> Selectivity to corresponding amino-derivative.

<sup>d</sup> Calculated from Fig. 5 [115].

<sup>e</sup> Calculated from Fig. 2 [116].

<sup>f</sup> Strongly basic APSDVB.

<sup>g</sup> Table I [117].

<sup>h</sup> SPSDVB-H.

<sup>i</sup> Fig. 2 [112].

<sup>j</sup> Fig. 1 [80].

<sup>k</sup> Fig. 2 [80].

<sup>l</sup> Fig. 2 [118].

<sup>m</sup> Table II [83].

<sup>n</sup> Fig. 1 [119].

<sup>o</sup> Fig. 2 [106].

<sup>p</sup> Fig. 5 [106].

<sup>r</sup> Fig. 4 [96].

<sup>s</sup> Selectivity to 4-aminophenol.

<sup>t</sup> Table II [120].



studied effects of metal alloying and of transition metal salts addition on the selectivity to CAn in the hydrogenation of *o*-CNB using PVP stabilised platinum and platinum–palladium colloids. Both activity and selectivity to CAn were increased by addition of  $\text{Ni}^{2+}$  salts to the reaction mixture [84] (66% selectivity at 100% conversion of CNB, 303 K, 0.1 MPa, average hydrogen consumption  $0.64 \text{ mol H}_2 / (\text{mol Pt s})$ , i.e.  $\text{TOF} = 38 \text{ min}^{-1}$ ). From an intensive survey on the influence of other metals ( $\text{Li}^+$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ ) on the PVP-Pt and PVP-Pt-Pd cluster catalysts (Table 5) [85] a catalytic system PVP-Pt-Pd modified with  $\text{Cr}^{3+}$  and  $\text{Co}^{2+}$  showed to be the best one yielding a 91% selectivity to *o*-CAn.

Exploitation of palladium catalysts in the hydrogenation of aromatic nitrocompounds is complicated by their deactivation. At the start of our own work on resin-supported metal catalyst, we used the hydrogenation of nitrotoluene as a test reaction for the estimation of the catalytic activity, but very soon we recorded changes in activity and palladium leaching after just one catalytic cycle [47]. A comprehensive discussion about the problem of deactivation with metal catalysts supported on functional polymers is reported in Section 5.

#### 4.1.4. Removal of oxygen from water

The process of catalytic removal of oxygen



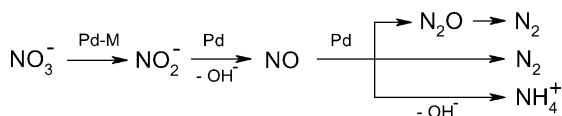
present in low concentrations in water to be used in heat-exchangers and for the production of steam is one of the very encouraging examples of industrial applications of metal catalysts supported on functional polymers [16]. Commercial Bayer deoxygenation catalysts are prepared mainly from cationic resins denoted as K 6333 [gel-type;  $(\text{P})-(\text{NR}_3)^+\text{Cl}^-$ ], VPOC 1045 OH/Cl free [gel-type;  $(\text{P})-(\text{NR}_3)^+\text{OH}^-$ ] and VP OC 1063 [macroporous;  $(\text{P})-\text{NR}_2$ ]. The palladium crystallites are located at the outer periphery of the beads. Therefore, the mass transport resistance is very low and the catalyst activity is high even at a relatively low average concentration of palladium (about 0.2 wt.%). The process of removal of oxygen is carried out in two stages: (i) absorption of hydrogen; and (ii) passage through a fixed-bed catalytic reactor operated at 80 bed volumes/h, pressure of  $\text{H}_2$  about

0.2 MPa at 25°C. When starting the process with the reactor filled with new catalyst, a minimal loss of palladium (about 2 mg/l) was observed during the first hour of operation, further losses were not detected.

The described catalysts are stable and some of them are purchasable from standard catalogues of chemical supplier [86].

#### 4.1.5. Removal of nitrates from drinking water

The high lifetime of palladium catalysts developed for the removal of oxygen from water as well as the easy preparation of metals dispersed on functional polymers inspired us [31] to prepare resin-based catalysts for the reduction of nitrates in water (Scheme 5). Almost all the catalysts reported to be active for this process are based on combinations of palladium with another metal [87]. Prusse et al. [88] offers a nice assessment of such catalysts; a combination of palladium with copper, tin or indium seems to yield the best catalytic activity and selectivity to nitrogen (the over-reduction to ammonia must be minimised). Besides a proper catalytic activity, mass transport hindrances must be minimised to allow the formed nitrogen to leave the metal surface. Starting from 4 mol% cross-linked SP5DVB commercially denoted as DOWEX, we have prepared [31] Pd-Cu catalysts containing either 2–0.5 wt.% Pd and Cu, respectively, or 4 and 1 wt.%, respectively. Along with catalytic activity, the formed ammonia was supposed to become trapped by the acid moieties present in the catalyst support. The latter assumption proved to be successful and it was possible to decrease the amount of nitrates from 100 (down) to <50 mg/l (the hygienic limit) with the amount of ammonia about 0.5 mg/l (the value of the hygienic limit). However, evaluation of the amount of ammonia trapped inside the polymer showed that the total selectivity to nitrogen was only about 60%. Moreover, leaching of metals was detected. Much lower leaching of metals was observed when a resin bearing carboxylic groups was used [89]. Pd-Cu catalysts supported on cationic



Scheme 5. The water phase reduction of nitrates.

Table 6

Water phase reduction of nitrates

Reference	Catalyst	<i>T</i> (°C)	<i>P</i> <sub>H<sub>2</sub></sub> (kPa)	<i>X</i> <sub>NO<sub>3</sub><sup>-</sup></sub> (%) <sup>a</sup>	Activity (mg <sub>NO<sub>3</sub><sup>-</sup></sub> /(g <sub>Pd</sub> s)) <sup>b</sup>	<i>S</i> <sub>NH<sub>4</sub></sub> (%) <sup>c</sup>	<i>S</i> <sub>NO<sub>2</sub><sup>-</sup></sub> (%) <sup>c</sup>
[88]	5% Pd/1.25% Cu/Al <sub>2</sub> O <sub>3</sub>	10	113	99 <sup>d</sup>	0.24 <sup>d</sup>	7.5 <sup>d</sup>	0
	5% Pd/1.25% Sn/Al <sub>2</sub> O <sub>3</sub>	10	113	99 <sup>e</sup>	1.18 <sup>e</sup>	1.5 <sup>e</sup>	0
[31]	4% Pd/1% Cu/S4-H <sup>f</sup>	25	46	52 <sup>g</sup>	0.015 <sup>g</sup>	38 <sup>h</sup>	0
	4% Pd/1% Cu/S4-Na <sup>f</sup>	25	46	46 <sup>g</sup>	0.013 <sup>g</sup>	40 <sup>h</sup>	46 <sup>h</sup>
[89]	3% Pd/0.7% Cu/(HEMA)	25	40	99	0.263	0.5	0.4
[90]	4% Pd/1% Cu/(D-A)	25	40	99	0.357	2.8	0.3

<sup>a</sup> Conversion of nitrates.<sup>b</sup> Average activity with respect to the 50% conversion of nitrates.<sup>c</sup> Molar selectivity to ammonia and nitrites with respect to the nitrogen.<sup>d</sup> Fig. 3 [88].<sup>e</sup> Fig. 4 [88].<sup>f</sup> SPSPDVB either in H<sup>+</sup>, or Na<sup>+</sup> form.<sup>g</sup> Table III [31].<sup>h</sup> Table IV [31].

resins [90] exhibited even higher activity and were sufficiently selective to nitrogen [89–91]. Selected results are reported in Table 6.

The faster hydrogenation rate observed over Pd-Cu/APSPDVB may be ascribed to two effects: (i) enhancement in the catalytic activity by nitrogen-containing functional groups of the resin; (ii) higher diffusivity of nitrates in the swollen cationic resins [92].

#### 4.2. Oxidation processes

Hanson et al. [93] prepared palladium and platinum catalysts supported on a macroporous SPSPDVB resin by ion-exchange of the sodium form of the resin with aminocomplexes of the metals. Analysis of XRPD patterns showed the above discussed effects of the reduction procedures (hydrogen, hydrazine, ethyl formate) on the average crystallite size and on their distribution: a low concentration of the reducing agent caused formation of an uneven distribution profile of the metal throughout the resin particles. Thus, in the case of hydrogen as the reducing agent, about 90% of palladium was located in an outer shell accounting for only 36% of the total volume of the polymer bead. These catalysts were tested in the liquid-phase oxidation of ethanol. The experiments were carried out in a stirred flask at 328 K with bubbling oxygen and out-gas of excess of oxygen and volatile products. The highest yield of acetaldehyde was achieved with the catalyst reduced

with ethyl formate, but even in this case, the dominant reaction was the total oxidation of the alcohol resulting in carbon dioxide as the main reaction product.

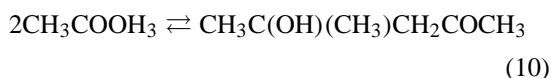
Lin et al. [49] studied the oxidation of ethanol in water over supported palladium catalysts (1 wt.%) in a fixed-bed reactor filled with 20 parts of glass beads and 1 part of a palladium metal catalyst at 95°C, 35.4 atm, air/EtOH molar ratio = 2.37, and WHSV = 2.4 g<sub>EtOH</sub>/(h g<sub>cat</sub>). They compared Pd/γ-Al<sub>2</sub>O<sub>3</sub> (strongly hydrophilic) and Pd/PSDVB (strongly hydrophobic macroporous resin) catalysts. They found the Pd/PSDVB catalyst to be about 25 times more active than Pd/γ-Al<sub>2</sub>O<sub>3</sub>. The higher activity of the former catalyst may be explained by the hydrophobicity of the PSDVB support which favours the desorption of water (one of the reaction products) from the surface, thus, allowing more fresh ethanol to gain access to the surface of the catalyst. However, the selectivity to acetaldehyde (the desired product) was only about 4% over the Pd/PSDVB catalyst in comparison with 35% over the Pd/γ-Al<sub>2</sub>O<sub>3</sub> catalyst. Moreover, relatively strong leaching of palladium from the Pd/PSDVB catalyst was monitored during the first 20 h of reaction. No leaching was recorded from the Pd/γ-Al<sub>2</sub>O<sub>3</sub> catalyst. Furthermore, in the case of Pd/PSDVB catalyst both dissolution and sintering of metal crystallites caused an increase in their average size from about 0.6 to 2 nm. The above-mentioned investigations are far too limited to draw some general conclusions about

the potentialities of resin-supported metal catalysts for oxidation reactions: much more work is needed in this area. A matter of concern which may have so far prevented the application of resin supports in this field is the stability of the support under the oxidative reaction conditions employed. Fortunately enough, some functional polymer supports which display excellent thermo-oxidative stability are commercially available. In particular, polybenzimidazoles [19,94] have already proved useful in oxidation processes carried out with metal catalysts or supported metal complexes (palladium, chromium), and may represent a useful starting point for the development of novel resin-supported metal catalysts.

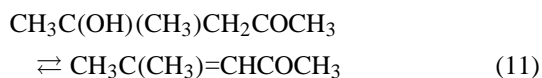
#### 4.3. Multifunctional catalysis

Multifunctional catalysis involves a combination of two or more reactions requiring different types of catalytic sites. Redox and acid–base catalysis is the most frequently used combination. A typical large-scale industrial application is the hydrocracking process which is carried out at temperatures about 400°C and >10 MPa pressure, i.e. conditions which seem to be far exceeding the field of applicability of resin-based catalysts [17]. On the other hand, resins appear to be ideally suited supports for multifunctional catalysts under milder conditions, due to their ease of functionalisation with different reactive groups. A good example of resin-supported multifunctional catalysis is the synthesis of methylisobutylketone (MIBK) from acetone [16,17]. Over palladium (about 0.1% w/w) doped macroporous SpSDVP (Bayer catalyst VP OC 1038) at temperatures about 130°C and 3 MPa working pressure the following three reactions proceed in a single reactor:

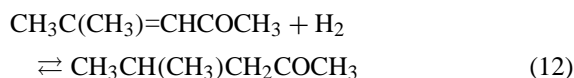
1. dimerisation of acetone to diacetone alcohol (DAA, 2-hydroxy-2-methyl-pentane-4-one):



2. elimination of water from DAA yielding mesityloxide (MSO, 2-methyl-2-pentene-4-one):

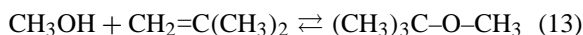


3. reduction of MSO to MIBK:



The process is commercial, yielding about 10<sup>4</sup> t per year of MIBK. Unfortunately, no data are available concerning the stability of the catalyst under the relatively drastic conditions employed in this reaction. Some speculation about this stability is given in the section devoted to deactivation of resin-based catalysts.

A similar multifunctional catalyst based on resin supports is also applied in the synthesis of methyl-*tert*-butyl ether from methanol and isobutene using directly the so called raffinate I fraction [17,18]:



The raffinate I also contains impurities of acetylenes, dienes, oxygenates and other compounds which could undergo reactions yielding macromolecular species. These species can stick to the surface of the acid catalyst and shorten its life. However, if the catalyst also contains a small amount of palladium and H<sub>2</sub> is added, the impurities are converted to less active monoolefines and other hydrogenation products [18]. Another advantage of this process lies in the direct treatment of the output (raffinate II) from the MTBE unit in an isomerisation unit [95], where due to increased content of butenes in the raffinate II the yield of isobutene could be increased, too.

Another industrially important reaction system is the condensation of amines with ketones coupled with the reduction of the formed Schiff base, which is applied, e.g. in the production of diphenylamine-based resin stabilisers [17]. Kljuev and Nasibulin [51] prepared in 98% yield alkylated anilines from aniline and isobutanal, or even directly from nitrobenzene and different aldehydes (isobutanal, hexanal, heptanal) with a Pd/APSDVB catalyst. An enhancement of the reaction rate of both hydrogenation and condensation steps by amino groups present in the catalyst was reported. The most active catalysts had pendant polyethyleneimine chains. Depending on the swellability and accessibility of the resin support, either mainly monoalkylated or dialkylated anilines were preferentially formed. In comparison with conventional Pd/C, the selectivity

to monoalkylated anilines was achieved in a much simpler way.

A novel challenge for multifunctional catalysis based on functional resin supports may become the synthesis of 4-aminophenol by the partial hydrogenation of nitrobenzene to *N*-phenylhydroxylamine and subsequent rearrangement to 4-aminophenol [96]. This is a reaction of great importance, in which the reduction of an aromatic nitrocompound is coupled with an acid-catalysed rearrangement (Scheme 4). The last two rows in Table 5 illustrate the activity and selectivity of two model catalytic systems based on Pt/C and on Pd/PVP colloids, respectively. In both these reactions, a conventional mineral acid is utilised. Metal catalysts supported on acidic ion-exchangers offer in principle the possibility of heterogenising both catalytically active moieties (the metal particles and the strongly acidic groups) on the same support, thus, limiting corrosion problems and facilitating catalyst recovery and reuse. Investigations on this approach are currently in progress in our group.

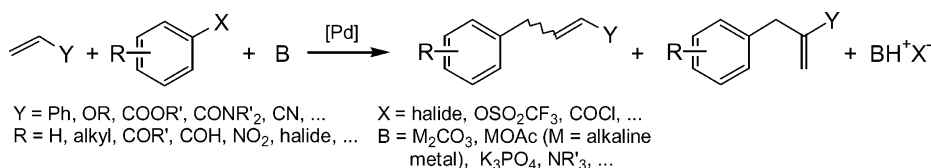
#### 4.4. Other reactions

Haag and Whitehurst [34] reported about reactions with carbon monoxide. For example, but-3-enoyl-chloride was prepared from allyl chloride and CO over Pd/SPSDVB at 100°C and 7 MPa. Under similar conditions methyl-but-3-enoate was also synthesised from allylmethyl ether. However, no information was reported about the stability of the catalyst. In any case, this process was probably not further developed.

Bergbreiter et al. [97] reported about various fine chemistry applications of resin-supported metal catalysts. They supported small palladium nanoparticles (about 2.5 nm) on phenylmethyl- or trimethylsilylmethyl-substituted PS. They tested these catalysts in allylic substitution reactions and found resin-based catalysts to be much more active than Pd/C catalysts.

An addition of triphenylphosphine enabled the carbonylation of phenyliodide followed by reaction with *n*-butanol yielding *n*-butylbenzoate (100°C, several days). Using a similar catalyst, the decarboxylation of allylic  $\beta$ -ketoesters to form  $\gamma,\delta$ -unsaturated ketones (important intermediates for chemical specialities) was easily achieved.

Polymer-supported palladium metal catalysts have been also employed in the arylation of alkenes with aryl halides (Heck reaction; Scheme 6) [98]. However, it needs to be remarked that in most instances “heterogeneous” palladium metal catalysts employed for this reaction mainly act as sources of soluble Pd(II) complexes, which are the true catalytically active species [98,99]. Most research efforts have been carried out by a Chinese research group, which utilised palladium on PS resins functionalised with nitrogen ligands such as phenantrolines [100–103]. Their preliminary results showed that this kind of catalysts were as active as the standard homogeneous catalyst precursor [Pd(OAc)<sub>2</sub>] in a number of Heck couplings of iodobenzene, if not somewhat superior. However, they also found that the catalysts underwent severe metal leaching (up to 74% of the metal was released into the liquid-phase after three runs), which limited the catalyst lifetime. This was attributed to the metal co-ordination of NBu<sub>3</sub> which was employed as the base. Indeed, the catalyst lifetime could be improved by using NaOAc as the base in *N,N*-dimethylformamide/water mixtures (2/1, v/v): under these conditions, up to six couplings of iodobenzene with styrene (and 10 for acrylamide) were carried out with the same catalyst batch with only a moderate decrease of the reaction yields. Most probably, under the latter conditions the leached Pd(II) species were co-ordinated by the resin-bound functional ligands, which prevented their release in solution. Thus, it seems that a viable way to have a catalytic system for this reaction which could be



Scheme 6. The Heck reaction.

properly defined “heterogeneous” is to devise a support able to co-ordinate, and therefore, to heterogenise the Pd(II) and Pd(0) species which occur in the different stages of the reaction cycle. We are currently engaged in the development of novel resin supports for this purpose.

## 5. Deactivation of polymer-based catalysts

The general deactivation processes of catalysts containing dispersed metals can be classified as follows:

1. sintering of metal crystallites;
2. formation of side products which poison the metal surface;
3. chemical changes involving the metal, e.g. oxidation, leaching, etc.;
4. chemical and physicochemical changes involving the support.

These modes of deactivation can occur both with inorganic and organic supports. However, changes involving the support are more peculiar for resin-based catalysts. Quite surprisingly, there is almost no quantitative information in the literature dealing with the deactivation of metal catalysts supported on functional resins. The reason for this could lie in the comparably low extent of application of resin-based catalysts in the industrial practice. Furthermore, the testing of these materials in academic research laboratories is usually not completed with appropriate long-time stability tests. In the course of the last years, we have started to investigate the problem of deactivation of resin-based metal catalysts more seriously, following our observations about the deactivation of palladium catalysts in the reduction of nitroaromatics [47,104]. Our attention has been focused on two aspects of deactivation, namely the dissolution and leaching of metal, and the degradation of the polymer support.

### 5.1. Dissolution of metal crystallites

Dissolution of metal crystallites supported on both inorganic and organic carriers is affected by factors such as the redox properties of the reaction system, the presence of modifiers and the chemical and morphological nature of the support.

The dissolution of metal particles occurs very rarely through the simple release of metal species in the zerovalent state. Thus, an oxidative reaction environment due, e.g. to an easy reducible substrate facilitates the dissolution of the metal, and therefore, the deactivation of the catalyst. Low concentrations of oxidising reactants can be employed to limit this phenomenon, but the concentration must be sufficiently high to achieve an acceptable reaction rate. Furthermore, the oxidation potential of the substrate (i.e. its hydrogenatability) as well as its affinity for the metal surface and consequent degree of chemisorption also play a role, as was documented by the low metal leaching observed in the hydrogenation of nitrophenols [105] and CNBs [106] in comparison to nitrotoluene.

In our laboratories, the deactivation phenomenon has been studied most intensively over palladium catalysts supported on commercial SP5DVB denoted as DOWEX (gel-type, 4–8 mol% cross-linked). A kinetic model involving both hydrogenation of nitrotoluene and dissolution of palladium was proposed [104]. Similarly to palladium catalysts supported on inorganic carriers [107], we have found a decrease in the dissolution of palladium at higher pressure of hydrogen and lower concentration of nitrocompound. The latter observation is fully capitalised in industrial practice with catalysts based on inorganic supports [108], where the deactivation in continuous reactors is decreased by immediately lowering the concentration of nitrobenzene upon dilution after entering the reactor operated at high conversion. A further decrease in the leaching was achieved by addition of other transition metals (e.g. cobalt) as modifiers of the metal phase [105].

The effect of the chemical and morphological nature of the support on metal dissolution can be rationalised in terms of the “redox” and/or ligand stabilising effect of the support on the metal particles, or in terms of the steric constraints of the support on the formation and transport of leached metal species.

So far, the “redox stabilising effect” of the support is not much elucidated even for inorganic based catalysts. Despite extensive investigation on the influence of the electronic and consequent electrical properties of the support on chemisorption processes [45,109], the understanding of the relevance of these parameters on the stability of supported metal particles is rather poor. In any case, charge transfer from the support to the metal may affect both its catalytic

activity (“structure–activity relationships”) and redox stability.

Resin supports can be generally considered as electrical insulators, even if there are some exceptions [71]. Thus, no particular electronic interactions between unfunctionalised resins and metal particles are expected, hence, no significant influence of the nature of the resin backbone on catalyst activity and stability. As a further consequence, the metal particles can be sometimes detached from these supports under reaction conditions [49]. However, suitable functional groups present on the polymer chains can interact strongly with the metal surface, thus, modifying its electronic structure, and therefore, its chemical properties. A good example of functional polymers able to stabilise metal crystallites are those bearing nitrogen moieties, e.g. amine, amide, imide, etc. [56,110].

As reported in our papers concerning the deactivation of palladium catalysts in the hydrogenation of substituted nitrobenzenes [26], the steric constraints exerted by the support may also significantly influence the deactivation process. If there is an equilibrium between the metal particle surface and leached oxidised metal species (for example, amine complexes in the reduction of nitrocompounds to aminocompounds), and steric obstacles do not allow their escape from the resin network, then deactivation is strongly hindered [26]. A similar stabilisation effect with increasing steric hindrances within the polymer support (i.e. with increasing cross-linking degree of the resin) was reported by Patel and Ram [111]. Of course, a drawback of this stabilisation method is the resulting lower accessibility of the metal particles and the subsequent lower rate of the process [26].

### 5.2. Deactivation due to degradation of the support

Inorganic supports change their properties usually at high temperatures (e.g. over 700°C for zeolites) or when they are employed in an aggressive environment like an acidic medium (e.g. oxides or hydroxides). Similar conditions also cause the degradation of organic supports, but additional modifications can be brought about by processes catalysed by the supported metal particles.

We have been able [112] to show that Pd/SPSDVB-H catalysts treated with hydrogen (0.5 MPa) in methanol and water undergo morphological changes which

could be easily monitored by ISEC measurements. A decrease in the volume fraction of the more cross-linked domains of the resin support accompanied by a corresponding increase in the volume fraction of the less cross-linked domains was detected. This was explained in terms of a partial hydrogenolysis of the polymer backbone catalysed by the supported metal. As it was shown by the determination of the rotational and translational mobility of dissolved species within the support, as well as by catalytic tests, this change in the morphology did not significantly influence the catalytic activity.

Furthermore, we have serendipitously discovered a rather peculiar kind of degradation of resin beads upon reduction of supports with a high loading of metal precursors (Fig. 5). The egg-yolk morphology observed is presumably due to “mass transport controlled hydrogenolysis” of the polymer backbone [113].

However, use of the reduced resin as catalyst under milder hydrogenation condition (0.05 MPa, room temperature) resulted in no further morphological changes.

In order to explain these experimental findings, we propose the hypothesis that metal particles in an oxidative or reductive environment may act as “hot stones” which “burn” the polymer chains of the support. This metal-catalysed degradation of the polymer network is favoured by high metal loading on the resin support, high concentration (pressure) of an oxidizing or reducing agent and high temperature. However, under proper conditions the resin-supported metal catalysts can be stable for months, or even years. Examples include industrial applications of these catalysts such as the removal of oxygen from water [16] and the one-pot synthesis of MIBK [16,17,114] which are carried out with a low metal loading of the catalyst and/or mild reaction conditions. There are indications in the literature that the extent of support degradation can be influenced also by other factors, such as the cross-linking degree of the support or the presence of functional groups interacting with the metal surface. However, more work is needed in order to rationalise these effects.

Finally, it must be remarked that in the course of the last years novel polymer supports have been developed which are much more resistant to degradation. Examples include aromatic and heterocyclic polymers like, e.g. polybenzimidazoles, poly(*p*-

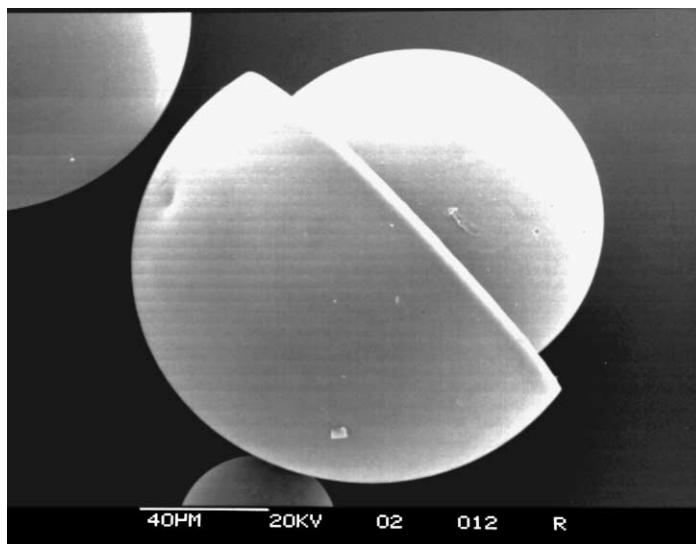


Fig. 5. Egg-yolk type particle obtained after the reduction (50°C, 1 MPa, 1 h) of Pd-Cu/SPSDVB-H resin containing 4 and 1 wt.% of palladium and copper, respectively [113].

phenylene-terephthalamide) [19], etc. Such materials enable the preparation of resin-supported metal catalysts for more demanding applications like, e.g. oxidations.

## 6. Conclusions

The scope of this review was to give a comprehensive overview of the potentialities of tailor-made catalysts based on metal nanoparticles supported on functional polymers. The interest in this kind of catalysts appears to be steadily increasing both from a fundamental and from a technological point of view. We hope that this contribution will convince more researchers committed to the development of new catalysts about the utility of such materials. Indeed, the combination of the intrinsic physicochemical features of the polymer support with the chemical properties of the polymer-bound functional groups and with the catalytic efficiency of the supported metal nanoparticles offers unique chances for the production of innovative catalysts in the commodities and fine chemical industry.

What could be the future of metal catalysts dispersed on functional polymers? First of all, the

active role of the polymer-bound functional groups as co-catalysts or promoters needs to be exploited in greater extent. PSDVB and APSDVB resins are so far the most frequently used functional supports, but usage of polyacrylates, polyimides, and other functional polymers is gradually growing. Supports bearing acidic functionalities have proved particularly suitable for multifunctional catalysts involving acid catalysis in one of the reaction steps. On the other hand, basic supports bearing nitrogen moieties appear more suitable for redox catalysis because they tend to promote the action of the metal nanoclusters by interaction of the functional groups with the metal surface. Additional functional groups, such as Lewis acid sites or polymer-bound metal ions or complexes need to be investigated in more detail.

All this should lead to the development of novel chemo-, regio- or even enantioselective catalysts, in which both non-chiral and chiral moieties could play a role.

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## References

- [1] G. Schmid (Ed.), *Cluster and Colloids: From Theory to Applications*, VCH, Weinheim, 1994.
- [2] C.N.R. Rao, G.U. Kulkarni, P.J. Thomas, P.P. Edwards, *Chem. Soc. Rev.* 29 (2000) 27.
- [3] J.D. Aiken III, R.G. Finke, *J. Mol. Catal. A: Chem.* 145 (1999) 1.
- [4] G. Schmid, L.F. Chi, *Adv. Mater.* 10 (1998) 515.
- [5] L.N. Lewis, *Chem. Rev.* 93 (1993) 2693.
- [6] G. Schmid, *Chem. Rev.* 92 (1992) 1709.
- [7] A. Henglein, *Chem. Rev.* 89 (1989) 1861.
- [8] M. Antonietti, F. Gröhn, J. Hartmann, L. Bronstein, *Angew. Chem. Int. Ed.* 36 (1997) 2080.
- [9] N.T. Whilton, B. Berton, L. Bronstein, H.-P. Hentze, M. Antonietti, *Adv. Mater.* 11 (1999) 1014.
- [10] A. Biffis, *J. Mol. Catal. A: Chem.* 165 (2001) 303.
- [11] Ch.-W. Chen, M.-Q. Chen, T. Serizawa, M. Akashi, *Chem. Commun.* (1998) 831.
- [12] W. Neier, in: K. Dorfner (Ed.), *Ion Exchangers*, De Gruyter (Walter), Berlin, 1991, p. 982.
- [13] A. Tanaka, T. Tosa, T. Kobayashi (Eds.), *Industrial Applications of Immobilised Biocatalysts*, Marcel Dekker, New York, 1993.
- [14] F.R. Hartley, *Supported Metal Complexes*, Reidel, Dordrecht, 1985.
- [15] S. Schlick, E. Bortel, K. Dyrek, *Acta Polym.* 47 (1996) 1.
- [16] R. Wagner, P.M. Lange, *Erdöl Erdgas Kohle* 115 (1989) 414.
- [17] K. Weissmermel, H.-P. Arpe, *Industrial Organic Chemistry*, 3rd Edition, VCH, Weinheim, 1997, p. 281, Chapter 11 (MIBK), p. 71, Chapter 3 (MTBE).
- [18] P.M. Lange, F. Martinola, S. Oeckel, *Hydrocarbon Processing*, December 1985, p. 51.
- [19] D.C. Sherrington, *Chem. Commun.* (1998) 2275.
- [20] E. Widgecke, in: D.C. Sherrington, P. Hodge (Eds.), *Synthesis and Separations using Functional Polymers*, Wiley, New York, 1988.
- [21] R. Arshady, *Adv. Mater.* 3 (1991) 182.
- [22] M. Zecca, R. Fisera, G. Palma, S. Lora, M. Hronec, M. Králík, *Chem. Eur. J.* 6 (2000) 1980.
- [23] A. Guyot, in: D.C. Sherrington, P. Hodge (Eds.), *Synthesis and Separations using Functional Polymers*, Wiley, New York, 1988.
- [24] R. Arshady (Ed.), *Desk Reference of Functional Polymers: Syntheses and Applications*, American Chemical Society, Washington, DC, 1997.
- [25] A.D. Pomogailo, V.S. Savostyanov, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.* C25 (1985) 375.
- [26] A. Primavera, B. Corain, M. Zecca, *J. Mol. Catal.: A Chem.* 108 (1996) 131.
- [27] G.I. Dzhardimalieva, A.D. Pomogajlo, *Kinet. i Katal.* 39 (1998) 893.
- [28] S.-M. Huang, B.-L. He, *React. Polym.* 23 (1994) 1.
- [29] S.A. Zavjalov, P.S. Voroncov, E.I. Grigorjev, G.N. Gerasimov, E.N. Golubeva, O.V. Zagorskaja, L.M. Zavjalova, L.I. Trachtenberg, *Kinet. i Katal.* 39 (1998) 905.
- [30] D. Belli Dell'Amico, S. Lora, A.A. D'Archivio, L. Galantini, A. Biffis, B. Corain, *J. Mol. Catal. A: Chem.* 157 (2000) 173.
- [31] D. Gašparovicová, M. Králík, M. Hronec, *Collect. Czech. Chem. Commun.* 64 (1999) 502.
- [32] P.W. Yen, T.Ch. Chou, *Appl. Catal. A: Gen.* 182 (1999) 217.
- [33] M. Králík, M. Hronec, S. Lora, G. Palma, M. Zecca, A. Biffis, B. Corain, *J. Mol. Catal.* 97 (1995) 145.
- [34] W.O. Haag, D.D. Whitehurst, *German Patents* 1800371 (1969); 1800379 (1969); 1800380 (1969).
- [35] A. Biffis, A.A. D'Archivio, K. Jerábek, G. Schmid, B. Corain, *Adv. Mater.* 12 (2000) 1909.
- [36] N. Toshima, in: T. Sugimoto (Ed.), *Fine Particles, Synthesis and Mechanism of Growth*, Marcel Dekker, New York, 2000, p. 430.
- [37] F. Pievet, in: T. Sugimoto (Ed.), *Fine Particles, Synthesis and Mechanism of Growth*, Marcel Dekker, New York, 2000, p. 460.
- [38] A. Drelinkiewicz, M. Hasik, M. Kloc, *J. Catal.* 186 (1999) 123.
- [39] M. Antonietti, S. Förster, S. Oestreich, *Macromol. Symp.* 121 (1997) 75.
- [40] K. Kimura, in: T. Sugimoto (Ed.), *Fine Particles, Synthesis and Mechanism of Growth*, Marcel Dekker, New York, 2000, p. 513.
- [41] K.J. Klabunde, *Free Atoms, Clusters and Nanoscale Particles*, Academic Press, New York, 1994.
- [42] M. Ohtaki, N. Toshima, M. Komiyama, H. Hirai, *Bull. Chem. Soc. Jpn.* 63 (1990) 433.
- [43] W. Yu, H. Liu, X. An, *J. Mol. Catal. A: Chem.* 129 (1998) L9.
- [44] B. Corain, K. Jerábek, M. Zecca, *J. Mol. Catal. A: Chem.* 177 (2001) 3.
- [45] G.A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, Wiley, New York, 1994.
- [46] N. Toshima, T. Yonezawa, *New. J. Chem.* (1998) 1179.
- [47] M. Králík, M. Hronec, V. Jorík, S. Lora, G. Palma, M. Zecca, A. Biffis, B. Corain, *J. Mol. Catal.* 101 (1995) 143.
- [48] M. Králík, V. Jorík, V. Kratky, unpublished results, 2001.
- [49] T.-B. Lin, D.-L. Chung, J.-R. Chang, *Ind. Eng. Chem. Res.* 38 (1999) 1271.
- [50] A. Biffis, H. Landes, K. Jerábek, B. Corain, *J. Mol. Catal. A: Chem.* 151 (2000) 283.
- [51] M.V. Kljuev, A.A. Nasibulin, *Kinet. i Katal.* 37 (1996) 231.
- [52] A. Biffis, B. Corain, Z. Cvengrošová, M. Hronec, K. Jerábek, M. Králík, *Appl. Catal. A: Gen.* 124 (1995) 355.
- [53] A. Biffis, B. Corain, Z. Cvengrošová, M. Hronec, K. Jerábek, M. Králík, *Appl. Catal. A: Gen.* 142 (1996) 327.
- [54] A.B.R. Mayer, J.E. Mark, *Colloid Polym. Sci.* 275 (4) (1997) 333.
- [55] J. Sabadie, J.-E. Germain, *Bull. Chim. France* 5/6 (1974) 1133.
- [56] Z.M. Michalska, B. Ostaszewski, J. Zientarska, J.W. Sobczak, *J. Mol. Catal. A: Chem.* 129 (1998) 207.



- [57] E. Sulman, Yu. Bodrova, V. Matveeva, N. Semagina, L. Cervený, V. Kurtc, L. Bronstein, O. Platonova, P. Valetsky, *Appl. Catal. A: Gen.* 176 (1999) 75.
- [58] K. Yamashita, H. Obana, I. Katsuta, US Patent 5,457,251 from Asahi Kasei Kogyo Kabushiki Kaisha, Japan, 10 October 1995.
- [59] P. Dini, D. Dones, S. Montelatici, N. Giordano, *J. Catal.* 30 (1973) 1.
- [60] S. Galvagno, A. Donato, G. Neri, D. Pietropaolo, P. Staiti, *React. Kinet. Catal. Lett.* 37 (1988) 443.
- [61] J. Struijk, M. d'Angremond, W.J.M. Lucas-de Regt, J.J.F. Scholten, *Appl. Catal. A: Gen.* 83 (1992) 263.
- [62] J. Struijk, R. Moene, T. van der Kamp, J.J.F. Scholten, *Appl. Catal. A: Gen.* 89 (1992) 77.
- [63] M. Hronec, Z. Cvengrošová, M. Králík, G. Palma, B. Corain, *J. Mol. Catal. A: Chem.* 105 (1996) 25.
- [64] M. Kralik, M. Kucera, M. Hronec, V. Macho, *SK Appl.* 0324/1995, 13 March 1995.
- [65] H. Gao, S. Liao, Y. Xu, R. Liu, J. Liu, D. Li, *Catal. Lett.* 27 (1994) 297.
- [66] H. Gao, Y. Xu, S. Liao, R. Liu, J. Liu, D. Li, D. Yu, Y. Zhao, Y. Fan, *J. Membr. Sci.* 106 (1995) 213.
- [67] C. Liu, Y. Xu, S. Liao, D. Yu, *J. Mol. Catal. A: Chem.* 157 (2000) 253.
- [68] C. Liu, Y. Xu, S. Liao, D. Yu, *Appl. Catal. A: Chem.* 172 (1998) 23.
- [69] C. Liu, Y. Xu, S. Liao, D. Yu, Y. Zhao, Y. Fan, *J. Membr. Sci.* 137 (1997) 139.
- [70] Ullman's Encyclopaedia of Industrial Chemistry, 6th Edition, Wiley, New York, 1998.
- [71] A. Drelinkiewicz, M. Hasik, M. Chozynski, *Mater. Res. Bull.* 33 (1998) 739.
- [72] G. Bombi, Laurea Thesis, University of Padova, 2001, in press.
- [73] R. Ricoveri, Laurea Thesis, University of Padova, 2001.
- [74] W. Yu, H. Liu, M. Liu, Q. Tao, *J. Mol. Catal. A: Chem.* 138 (1999) 273.
- [75] R.L. Augustine, *Catal. Today* 37 (1997) 419.
- [76] H.U. Blaser, M. Studer, *Appl. Catal. A: Gen.* 189 (1999) 191.
- [77] B. Coq, F. Figueras, *Coord. Chem. Rev.* 178/180 (1998) 1753.
- [78] E. Bamberger, H. Büsdorf, H. Sand, *Ber.* 31 (1898) 1513.
- [79] D. Groskova, Ph.D. Thesis, CHTF Bratislava, 2000.
- [80] M.G. Abdullajev, A.A. Nasibulin, M.V. Kljuev, *Zh. Org. Chim.* 33 (1997) 1759.
- [81] M. Lauwiner, R. Roth, P. Rys, *Appl. Catal. A: Gen.* 77 (1999) 9.
- [82] E. Auer, A. Freund, M. Gross, R. Hartung, P, in: F.E. Herkes (Ed.), *Catalytic of Organic Reactions*, Marcel Dekker, New York, 1998, p. 552.
- [83] Z. Yu, Sh. Liao, Y. Xu, B. Yang, D. Yu, *J. Mol. Catal. A: Chem.* 120 (1997) 247.
- [84] X. Yang, H. Liu, *Appl. Catal. A: Gen.* 164 (1997) 197.
- [85] X. Yang, H. Liu, H. Zhong, *J. Mol. Catal. A: Chem.* 174 (1999) 55.
- [86] Lewatit Catalysts, Fluka Catalogue, 1999/2000, p. 834.
- [87] K.D. Vorlop, T. Tacke, *Chem.-Ing.-Tech.* 61 (1989) 836.
- [88] U. Prusse, M. Hahnlein, J. Daum, K.D. Vorlop, *Catal. Today* 55 (2000) 79.
- [89] G. Radicova, Thesis, Slovak University of Technology, Bratislava, 2001.
- [90] I. Jesikova, Thesis, Slovak University of Technology, Bratislava, 2001.
- [91] M. Kralik, D. Gasparovicova, in: *Proceedings of the CHISA'2000*, Prague, 27–31 August, p. 132.
- [92] P. Mears, in: J. Crank, G.S. Park (Eds.), *Diffusion in Polymers*, Academic Press, New York, 1968, p. 373.
- [93] D.L. Hanson, J.R. Katzer, B.C. Gates, G.C.A. Schutt, *J. Catal.* 32 (1974) 204.
- [94] N.H. Li, J.M.J. Frechet, *React. Polym.* 6 (1987) 311.
- [95] V. Macho, M. Kralik, L. Jurecek, E. Jurecekova, J. Balazova, *Appl. Catal. A: Gen.* 203 (2000) 14.
- [96] C.V. Rode, M.J. Vaidya, R.V. Chaudhari, *Organ. Proc. Res. Dev.* 3 (1999) 465.
- [97] D.E. Bergbreiter, B. Chen, D. Weatherford, *J. Mol. Catal.* 74 (1992) 409.
- [98] A. Biffis, M. Zecca, M. Basato, *J. Mol. Catal. A: Chem.* 173 (2001) 249.
- [99] A. Biffis, M. Zecca, M. Basato, *Eur. J. Inorg. Chem.* 5 (2001) 1131.
- [100] Z. Zhuangyu, H. Hongwen, K. Tsi-Yu, *React. Polym.* 9 (1988) 249.
- [101] Z. Zhuangyu, H. Hongwen, K. Tsi-Yu, *React. Polym.* 12 (1990) 229.
- [102] Z. Zhuangyu, P. Yi, H. Hongwen, K. Tsi-Yu, *Synthesis* (1991) 539.
- [103] P. Yi, Z. Zhuangyu, H. Hongwen, *J. Mol. Catal.* 62 (1990) 297.
- [104] R. Fišera, M. Králík, J. Annus, V. Krátky, M. Zecca, M. Hronec, *Coll. Czech. Chem. Commun.* 62 (1997) 1763.
- [105] M. Kralik, V. Kratky, M. Hronec, M. Zecca, B. Corain, *Stud. Surf. Sci. Catal.* 130 (2000) 2321.
- [106] V. Kratky, M. Kralik, M. Hronec, M. Zecca, *Petroleum Coal* 42 (2000) 28.
- [107] A.J. Bird, D.T. Thompson, in: W. Jones (Ed.), *Catalysis in Organic Synthesis*, Academic Press, New York, 1980, p. 61.
- [108] B. Amini, *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Edition, Vol. 2, Wiley, New York, 1992, p. 433.
- [109] J.E. Germain: *Catalyse Heterogene*, Dunod, Paris, 1959.
- [110] B. Corain, M. Kralik, M. Zecca, A. Biffis, 2001, unpublished results.
- [111] D.R. Patel, R.N. Ram, *J. Mol. Catal. A: Chem.* 130 (1998) 57.
- [112] M. Králík, R. Fišera, M. Zecca, A.A. D. Archivio, L. Galantini, K. Jerabek, B. Corain, *Coll. Czech. Chem. Commun.* 63 (1998) 1074.
- [113] M. Kralik, B. Corain, M. Zecca, *Chem. Papers* 54 (2000) 254.
- [114] J. Braithwaite, *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Edition, Vol. 14, Wiley, New York, 1992, p. 992.

- [115] H.J. Janssen, A.J. Kruithof, G.J. Steghuis, K.R. Westerterp, *Ind. Eng. Chem. Res.* 29 (1990) 1822.
- [116] G. Neri, M.G. Musolino, C. Milone, S. Galvagno, *Ind. Eng. Chem. Res.* 34 (1995) 2226.
- [117] M.V. Kljuev, A.A. Nasibulin, E.F. Vajnschetjn, *Neftechimija* 33 (1993) 261.
- [118] C.V. Rode, R.V. Chaudhari, *Ind. Eng. Chem. Res.* 33 (1994) 1645.
- [119] V. Kratky, M. Hronec, M. Kralik, in: *Proceedings of the XXXII Symposium on Catalysis, Prague, 2000*, p. OP11.
- [120] Y. Gao, F. Wang, S. Liao, D. Yu, *React. Kinet. Catal. Lett.* 64 (1998) 351.